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Thomas Beddoes (1760–1808)

For the teacher to be forgotten and the pupil remembered is not unusual, but sometimes the brilliance of the student has unduly overshadowed the talent of his master. Such was the case with Thomas Beddoes, from whom the young Cornishman Humphry Davy certainly learnt much at a formative stage in his career. Short though it was, Davy's appointment as superintendent of the Medical Pneumatic Institute at Clifton, Bristol, was an important episode in his career. John Davy, his brother, wrote: 'If this situation had been created purposely for him it could not have been more suitable for the bent of his genius, or better adapted for calling into activity and developing fully the powers of his mind.' It may well be true that Beddoes's greatest discovery was Davy, but nevertheless he was himself a significant figure in his own time, progressive-minded in an age when it was dangerous to be so, and influential in literature as well as in science and medicine. Indeed, the very breadth of his interests seems to have denied him more lasting fame. Davy's own assessment was that Beddoes 'had talents which would have raised him to the pinnacle of philosophical eminence if they had been applied with discretion'.

Beddoes was born in Shropshire two hundred years ago, and entered Pembroke College, Oxford, at the age of sixteen. Here, in addition to his classical studies, he not only taught himself French, German, and Italian, but became interested also in botany, mineralogy, and chemistry: within a few years he acquired considerable knowledge of the means of handling gases—'airs' as they were then called—and of their chemistry; he was later to turn this knowledge in a new direction by investigating the medical uses of gases. However, by 1779 his interest in chemistry had diminished and he had turned to medicine, and two years later he went to London to study anatomy under John Sheldon: he completed his medical studies at Edinburgh, where he remained until the summer of 1787.

The wide range of Beddoes's interests soon became apparent. His literary work commenced with a translation of the *Dissertazioni* of Spallanzani (1729–99), whose work was then little known in England. He also published translations of the chemical works of Tobern Bergman (1735–84) and Scheele (1742–86). The autumn of 1787 saw him on a tour of Europe: clearly his chemical interests had revived, for he visited Lavoisier and became friendly with Guyton de Morveau. Returning to Oxford, whose D.M. degree he had obtained in 1786, Beddoes was in 1788 appointed Reader in Chemistry, receiving no salary apart from the fees paid by such students as voluntarily attended his lectures. He attracted large classes; the largest in the university, he claimed, since the thirteenth century.

These were, of course, times when chemistry was undergoing a revolution–the overthrow of the phlogiston theory–and the change in Beddoes's opinions can be clearly traced in his writings. In his translations of Bergman and Scheele he accepted the phlogiston theory of Stahl. In 1789 he wrote to William Higgins about 'Dr Priestley's late admirable experiments' which had 'reestablished the existence of phlogiston'. In the following year he published an account of the work and theories of the then neglected chemist John Mayow (1641–79), under the title 'Chemical Experiments and Opinions Extracted from a Work published in the Last Century'. This aroused considerable interest; it also led to some controversy between Beddoes and some of the French chemists, especially Fourcroy. According to Beddoes, Mayow had 'clearly presented the notion of phlogiston, which rendered the name of Stahl so celebrated'. By November 1791, however, questions of priority in formulating the phlogiston theory were of minor interest, for Beddoes had come to accept Lavoisier's theory.

Beddoes's wide circle of friends extended far outside Oxford. Among them were some of his most distinguished contemporaries, including several members of the Lunar Society, of Birmingham, a group of natural philosophers so called because, for convenience in returning home, they met at the time of the full moon; his friends included Joseph Priestley, Erasmus Darwin, the Wedgwoods, William Withering, Matthew Boulton, and James Watt. The Lunar Society had links, through Benjamin Franklin, with the revolutionaries in both France and America, and these sympathies led some of the members into trouble. A dinner held by James Keir, a chemical manufacturer, to celebrate the second anniversary of the fall of the Bastille led to the riot in which Priestley's house was destroyed. During the long vacation of 1792 Beddoes circulated a leaflet sympathetic to the French Revolution, which was coldly received

by many of his colleagues at Oxford; he resigned his readership and left the university.

He moved to Clifton and there worked hard to build up a medical practice while continuing his writing; at the same time he resumed his interest in the medical uses of gases, particularly oxygen, 'fixed air' (carbon dioxide), and 'hydrocarbonate' (water-gas). In 1794 was published his 'Considerations on the Medical Use of Factitious Airs and on the Manner of Obtaining them in Large Quantities'; this was in two parts, the first by Beddoes and the second by James Watt, who had collaborated with him in the design of pneumatic apparatus.

In this book he developed further his ambitious ideas for the establishment of a Medical Pneumatic Institution at which the 'airs' would be administered by a salaried superintendent under the supervision of a physician. This position of superintendent was eventually filled in October 1798 by the nineteen-year-old Humphry Davy. That the Institution actually came into existence in that year was largely due to the generosity of Thomas Wedgwood and other friends, including Richard Kirwan, the Irish chemist.

For Davy, the apothecary's poor apprentice, the move to Clifton was a major step in his career. It arose from his becoming known to friends of Beddoes, particularly Davies Giddy, a wealthy landowner and amateur of science who later (as Davies Gilbert) became President of the Royal Society. Another relevant factor was that James Watt's younger son, Gregory, had gone to Penzance for the sake of the climate and, through lodging with Davy's widowed mother, had become a close friend of Davy. It is not surprising, therefore, that when Davy wanted an opinion on his speculative essay 'On the Nature of Heat and Light' and on his first experiments in chemistry he should have turned to Beddoes. The latter formed a high opinion of the young man's work, and the first scientific paper Davy published appeared in Beddoes's 'Contribution to Physical and Medical Knowledge mainly from the West of England'.

Davy found Beddoes abrupt on first acquaintance but very charming to those he really liked. In his first letter home he wrote: 'Dr Beddoes is . . . uncommonly short and fat, with little elegance of manner and nothing characteristic externally of genius and science.' But within a few weeks he was writing: 'I am quite naturalised into the family and I love them the more I know them.' Davy resumed his work on nitrous oxide under Beddoes's direction, and naturally the effects of breathing the gas were studied. Davy first breathed enough to experience its effects in April 1799, and he observed the anaesthetic value of the gas in connection with the painful arrival of his own wisdom teeth. Unfortunately the immense medical possibilities of his observations, realized half a century later, were lost sight of in the fashionable 'laughing gas' craze, which Beddoes rather encouraged because of its publicity value to his Institution. However, Davy was already turning his attention to the new science of 'galvanism'; Beddoes had been interested in this for some years and had constructed voltaic piles for his own use. Davy built a pile for himself, and with it he made several important observations, described in papers in 'Nicholson's Journal'.

Beddoes's influence on Davy was by no means only in encouraging him and assisting him in his chemical experiments, for his wide circle of friends at Clifton was not even predominantly scientific. Among them was R. L. Edgeworth, a well-informed amateur scientist, who had helped placate local opposition to the work with 'noxious' gases. In 1794 Beddoes married Edgeworth's daughter Anna, sister of Maria, the novelist; their elder son was Thomas Lovell Beddoes, the poet. Beddoes's home in Clifton became the focal point for the local literary society, which included the poets Southey, Coleridge, and Wordsworth. Davy met them all, and his own considerable poetical talent found an outlet in 'The Sons of Genius', published in Southey's 'Annual Anthology'. Although Davy enjoyed this society for only sixteen months before going to the newly founded Royal Institution in London as Director of the Laboratory, it was undoubtedly valuable to him in bridging the gulf between his humble life in Penzance and the demands of fashionable circles in London.

The character of the Pneumatic Institution changed steadily after Davy's departure. In two years the 'pneumatic practice' was abandoned, and eventually the building was used as a clinic for preventive medicine. Although it contributed little of lasting scientific value, its importance should not be under-rated: it was one of the first of the now familiar research institutes. Beddoes moved to London and there built up a considerable medical practice before his death on 24th December 1808.

The neurosecretory system of the diencephalon

W. BARGMANN

This article describes the neurosecretory cells of the diencephalon, whose varied functions include the regulation of water-retention, blood pressure, muscular contraction of the uterus, and the release of milk by the mammary gland. It discusses also the way in which the system may influence the activity of the anterior lobe of the pituitary gland. Apart from its general physiological and biochemical interest, knowledge of the neurosecretory system of the diencephalon is of practical importance in relation to the disease diabetes insipidus.

Until about seventy years ago, virtually nothing was known of the function of the part of the brain that Galen had named the hypophysis cerebri. Today every student of biology and medicine knows that the hypophysis, or pituitary, which is divided into anterior, middle, and posterior lobes, is a complex endocrine organ with a surprising number of activities, some clearly identified. For example, the pituitary produces hormones which control the activity of other endocrine glands, such as the thyroid, the suprarenals, and the corpus luteum of the ovary.

Until recently, a particularly puzzling feature of the pituitary was that, although hormones can be extracted from its posterior lobe, the neurohypophysis, this lobe contains no cells having the morphological characteristics of secretory cells, such as are found in great numbers in the anterior lobe. Two hormones, vasopressin and oxytocin, have so far been extracted from the posterior lobe; both are octapeptides with similar configurations. Vasopressin reduces urine output and so guards the organism against excessive water loss; it also causes a rise in blood pressure. It has been shown experimentally that the posterior lobe influences water retention in representatives of all classes of vertebrates [18]. Oxytocin produces contraction of the smooth muscle of the uterus and also of the contractile cells of the mammary gland; it thus causes release of milk in the lactating animal, the 'milk let-down.'

As has been said, the posterior lobe of the pituitary contains no typical glandular cells such as one finds in other endocrine glands. Microscopic examination of preparations of the neurohypophysis discloses a very dense felt-like network of fine nerve fibres, lying close to the walls of the capillaries. One can also see branching, non-nervous glial cells called pituicytes. Both these cells and the nerve fibres must be considered as potential producers of hormones. There has been no verification of the claim that cultures of cells of the posterior lobe in which pituicytes had multiplied produce a substance with an antidiuretic action [21]. The interest of investigators has therefore been concentrated on the nervous network in the posterior lobe as the next most likely source of vasopressin and oxytocin.

Any theory that seeks to establish a neural origin for the posterior-lobe hormones must establish:

(1) the origin of the nerve fibres that end in the posterior lobe, and

(2) whether these fibres are clearly differentiated, functionally and morphologically, from other nerve fibres.

As early as 1899 Cajal pointed out that the fine nerve fibres of the neurohypophysis are extensions of diencephalic neurons, which lie in various cell groups behind the optic chiasma. According to our present knowledge, the fibres arise in two nuclei of the hypothalamus, the supraoptic and the paraventricular nuclei (figure 13). In lower vertebrates these two nuclei are represented by a single nucleus, the nucleus praeopticus. Further, short nerve-fibres extend to the posterior lobe from nuclei situated in an eminence in the floor of the diencephalon known as the tuber cinereum. These nuclei are called the tuberal nuclei.

The presence of granules and colloid droplets in the cytoplasm has long been recognized [39] as a characteristic feature of the perinuclear region of the supraoptic and paraventricular (or praeoptic) nuclei. These cellular inclusions are indicative of secretory activity, which has led to the term 'glandular nerve cells'. Single chains of secretory droplets, that is, of neurosecretion, could be

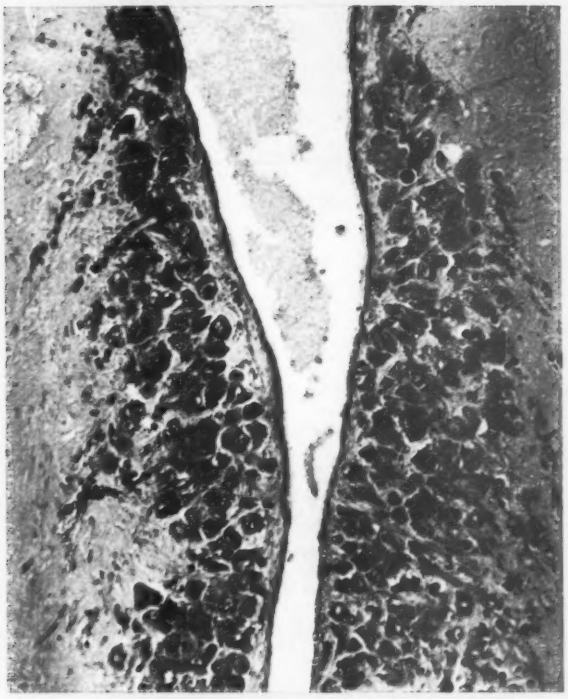


FIGURE 1 – *Nucleus praeopticus of a teleost fish* (Gadus virens), *showing colloidal droplets (black). Transverse section through the diencephalon in the central region of the ventricle. Stain: chrome-alum/haematoxylin.* (× *approx.* 100)

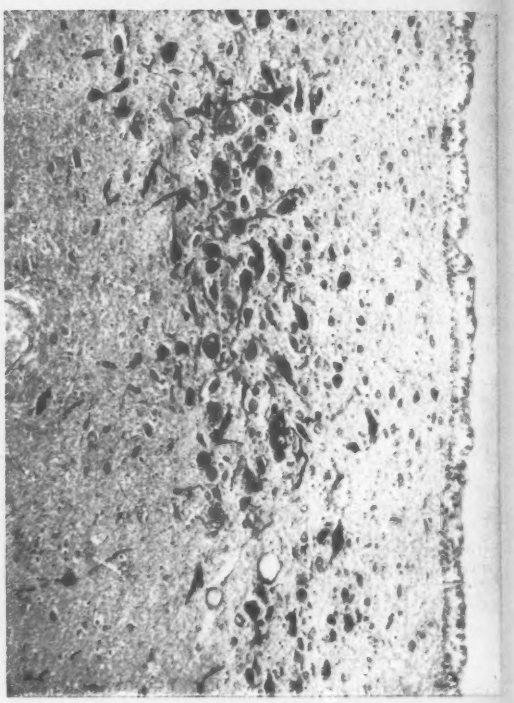


FIGURE 2 – *Frontal section through the paraventricular nucleus of a dog, showing nerve cells containing neurosecretion (black). On the right is the third ventricle. Stain: chrome-alum/haematoxylin.* (× *approx.* 100)

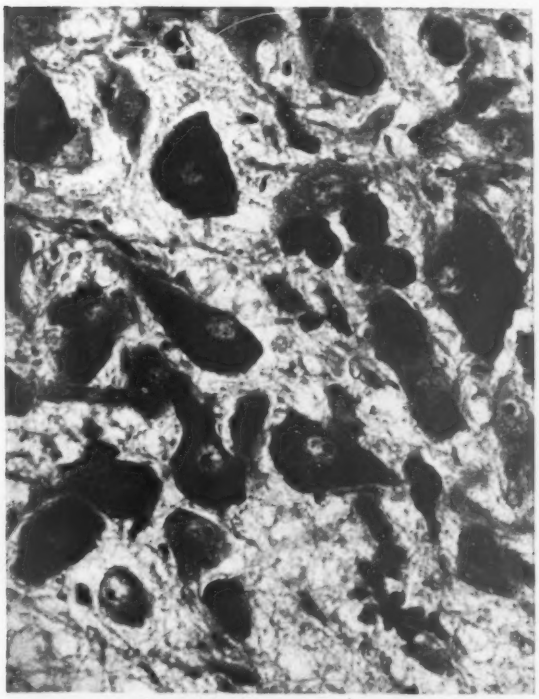


FIGURE 3 – *Group of nerve cells in the supraoptic nucleus of a dog, showing neurosecretion (black). Stain: chrome-alum/haematoxylin.* (× *approx.* 500)

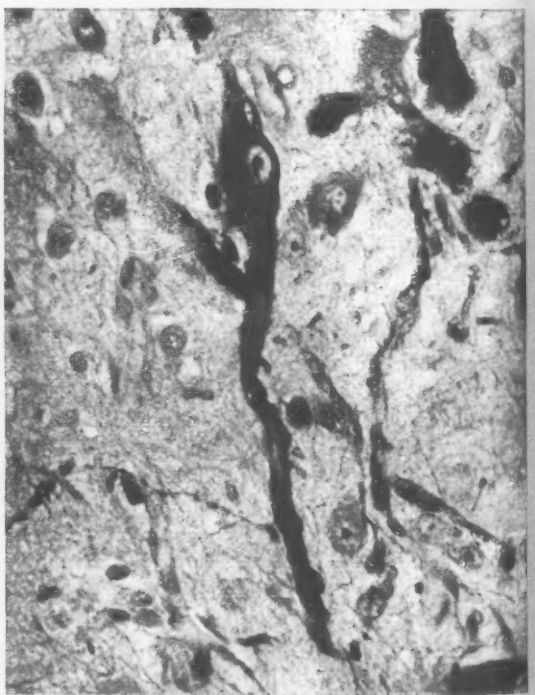


FIGURE 4 – *Nerve cell containing neurosecretion and showing a process with secretory contents, from the supraoptic nucleus of a dog. Stain and magnification as in figure* 3.

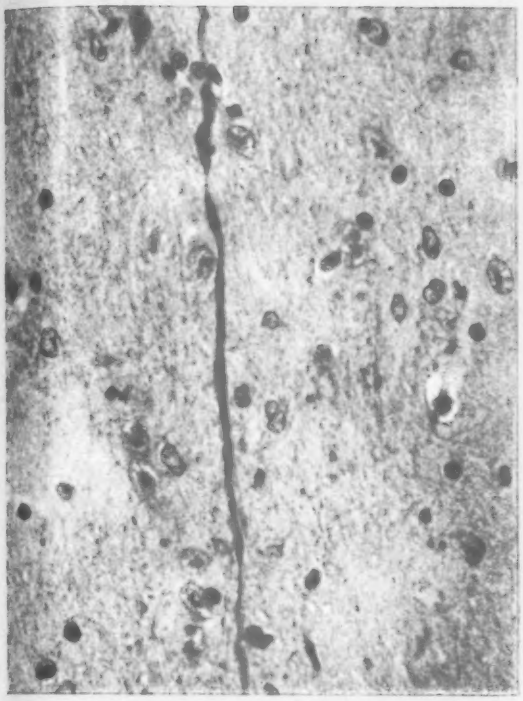


FIGURE 5 – *Single nerve fibre containing neurosecretion, from the diencephalon of a dog. Stain and magnification as in figure* 3.

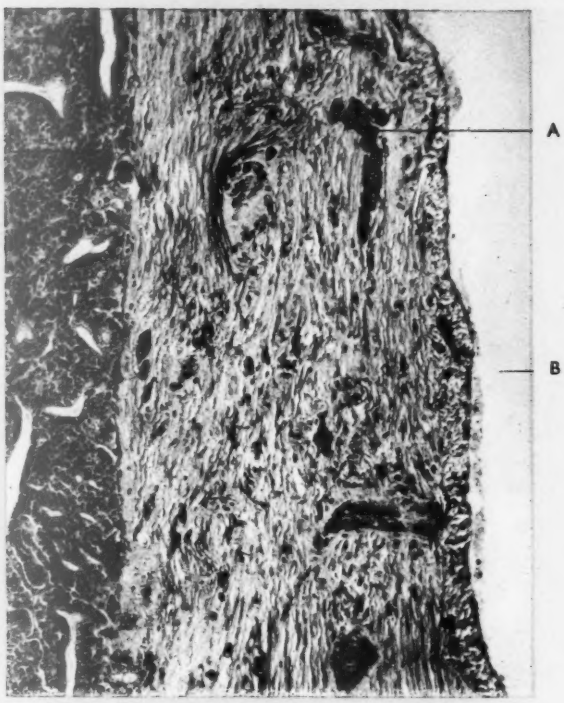


FIGURE 6 – *Parallel nerve fibres containing secretion (A), from the neurosecretory pathway in the hypophysial stalk (infundibular wall) of a dog. Left, part of the adeno-hypophysis; right, ventricle (B). Fibre swellings containing secretion appear black. Stain: chrome-alum/haematoxylin.* (× *approx.* 100)

FIGURE 7 – *Posterior lobe of pituitary of a dog, showing small neurosecretory particles (black). Neurosecretory contents appear light. Stain: chrome-alum/haematoxylin.* (× *approx.* 480)

FIGURE 8 – *Posterior lobe of the pituitary of a cat, showing concentration of neurosecretion near the capillaries. Stain and magnification as in figure* 7. (× *approx.* 480)

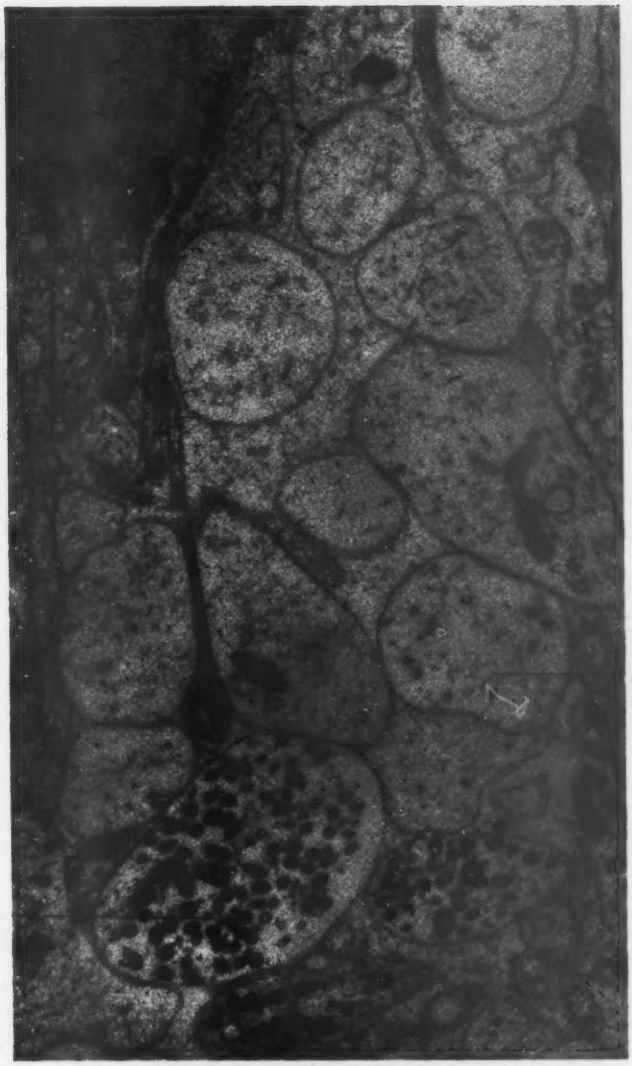


FIGURE 9 – *Electron micrograph of the neurohypophysis of a teleost fish* (Gadus morrhua), *showing nerve fibres that are partly free of secretion* (*A*) *and partly contain granules* (*B*). (× 14 000)

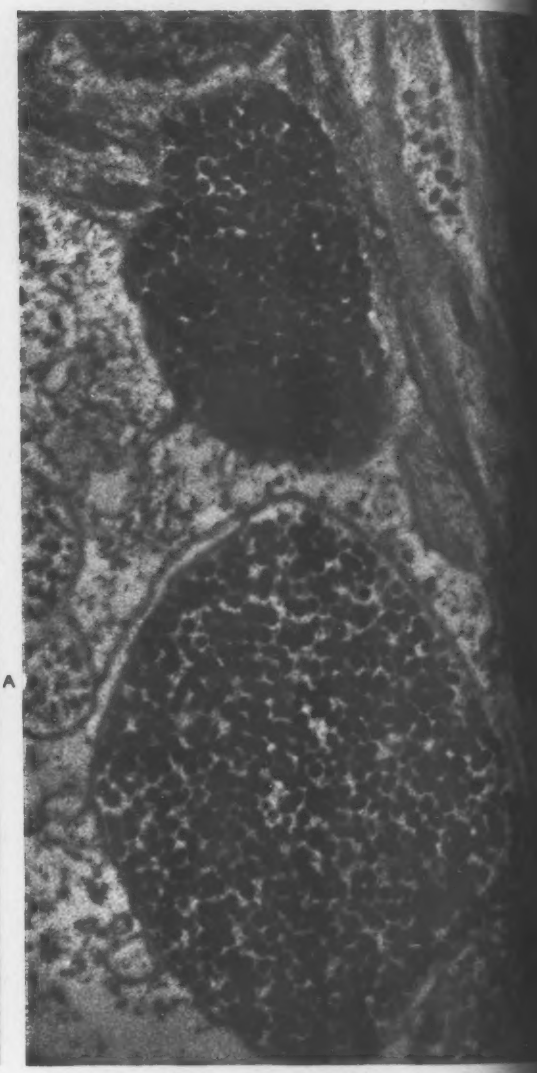


FIGURE 10 – *Electron micrograph of two nerve fibres cut transversely in the neurohypophysis of a teleost fish* (Gadus morrhua) *showing numerous neurosecretory granules.* (× 14 000)

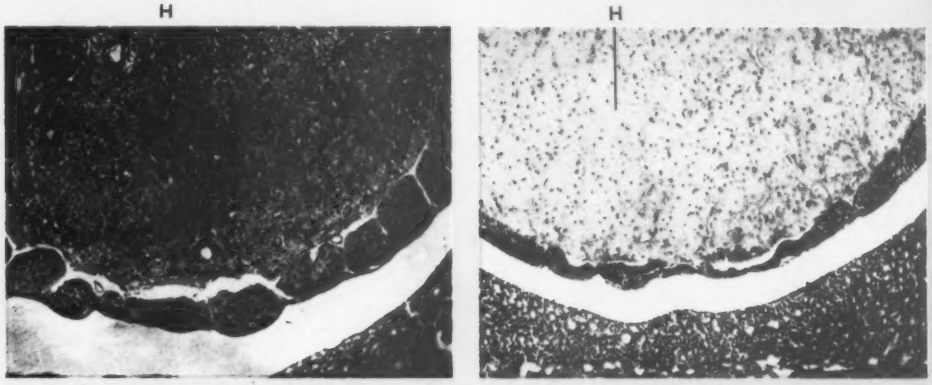


FIGURE 11 – *Posterior lobe of the pituitary* (*H*) *of a rat* (*left*) *with high neurosecretory content and* (*right*) *after the animal had suffered severe water loss: the lobe is then free of neurosecretion* [26]. *Stain: chrome-alum/haematoxylin.* (× 74)

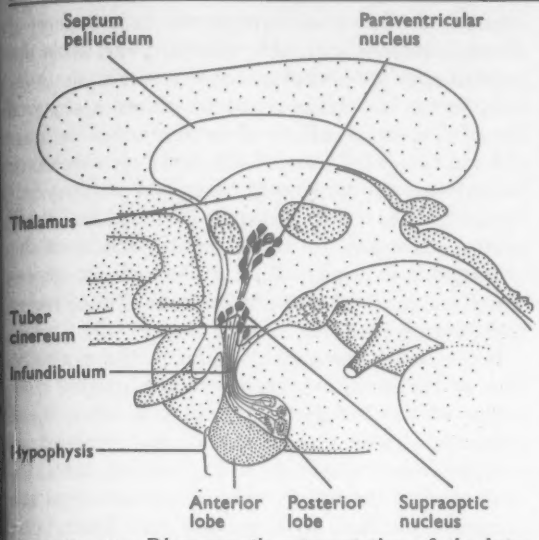


FIGURE 12 – *Diagrammatic representation of the hypothalamo-pituitary neurosecretory pathway in man: median longitudinal section with position of the supraoptic and paraventricular nuclei superimposed. The processes of the secretory nerve cells extend into the posterior lobe.* [39]

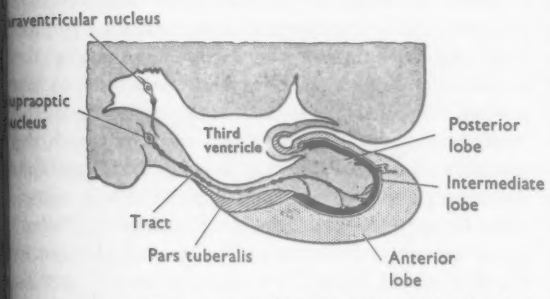


FIGURE 13 – *Course of the hypophysial tract in the dog.*

demonstrated in the unmyelinated fibres directed towards the hypophysis, but it was not possible to trace this material into the terminal nerve-plexus in the posterior lobe. During the last decade, however, we have been able [3] to demonstrate a neurosecretory pathway by means of a selective histological staining technique which shows the secretory contents throughout the pathway, that is, from the diencephalic nuclei, through the infundibular wall, to the neurohypophysis (figures 1–8). Today we know other methods than the use of the chrome-alum/haematoxylin stain that was originally used to demonstrate the neurosecretory neuron [41, 42]. Even the finest nervous networks in the posterior lobe contain neurosecretory granules, but granules much smaller than those found in the fibre portions close to the brain or in the bodies of the neurosecretory cells. A characteristic feature of the fibres of the neurosecretory pathway are well-defined, often spherical enlargements, rich in secretion. They correspond to the long-known Herring bodies which, however, were wrongly taken to be isolated structures. It is not yet known whether the nerve cells of the mammalian nuclei tuberis actively secrete.

The submicroscopic structure of the secretory neurons of the diencephalon can also be distinguished from that of other nerve cells. Electron micrographs (figures 9 and 10) show numerous dense granules [32] which can be traced as far as the nerve endings in the posterior lobe. Their diameter is 1200–1800 Å in mammals and 1500–3000 Å in lower vertebrates [5]. Accumulations of such particles form the basis for the picture of neurosecretion revealed by the optical microscope. Larger drops arise through the confluence of these granules.

The phenomenon of neurosecretion must be considered from the point of view of general cytology. Gland cells, for example in the pancreas, form secretory granules in the nuclear region of the cytoplasm which is characterized by special lamellated structures, namely the ergastoplasm and the Golgi apparatus. Since both of these lamellated structures are found concentrated in the nuclear region of the glandular nerve cells, while the neurosecretion occurs in the nuclear region and also in the part of the processes extending away from the cell and in its terminal arborizations in the posterior lobe, the following question arises. Does the nuclear region of the neuron (the perikaryon) produce the granules, and are these then transported to the posterior lobe? If this is so, the supraoptic and paraventricular nuclei can be regarded as the site of production; the nervous processes as the transport path; and the terminal arborizations as the storage site for the neurosecretion.

Observations by P. Weiss on an axonal flow away from the centre of the cell in non-secretory nerve fibres favour such a view. Further, tissue cultures of living neurons from the paraventricular nucleus of the dog have shown a distal movement of granules [21]. Also, after division of the hypophysial stalk—that is, interruption of the neurosecretory pathway—there is a thickening of the centrally placed nerve fibres accompanied by an increase in neurosecretion and a loss of the neurosecretory material in the distal parts of the fibre pathway: this picture, which has also been seen after path section in man, can be regarded as a block at the site of interruption [21, 46]. Finally,

observations on the hypophysial stalk of a teleost fish [10], and investigations of analogous neurosecretory pathways in invertebrates (in which neurosecretion plays an important part), are further evidence for a transport of neurosecretions from the nuclear region of the cell to the endings.

Thus it appears that neurosecretory cell groups in the diencephalon are connected to the posterior lobe of the hypophysis by their processes. The posterior lobe does not appear to be the site of formation of the secretion, but to be a storage organ for the granules, which can be selectively stained and have a characteristic appearance under the electron microscope. The posterior lobe releases the hormones vasopressin and oxytocin into the blood stream when they are needed. The development of a production site, a transport path, and a storage organ can also be recognized in other neurosecretory hormonally active systems in invertebrates, such as insects and crustacea, and in vertebrates [14, 38].

FUNCTIONAL SIGNIFICANCE

We shall now consider the functional significance of this system. In this connection earlier investigations of the control of water retention are relevant. Classical experiments of H. W. Magoun and of S. W. Ranson, C. Fisher, and W. R. Ingram [34, 35] on mammals showed that cutting the stalk of the pituitary, the infundibulum (figure 12), is followed by a heavy flow of urine. It has also been known for a long time that diabetes insipidus in man—that is, a water loss that seriously threatens the organism—always results from destruction of, or damage to, the posterior lobe or the stalk of the pituitary. Further, diabetes insipidus has also been observed in man when the supraoptic and paraventricular nuclei (figure 12) are insufficiently developed [12]. On the other hand, the urine output is reduced if the osmotic pressure of the blood in the capillary bed of the supraoptic nucleus is above normal. This has been shown by E. B. Verney's elegant experiments on the dog [47]. Verney considers that in the region of this nucleus there are receptors, the excitation of which causes a release of antidiuretic substance from the posterior lobe. Even after injection of acetylcholine into the supraoptic nucleus of the dog, the flow of urine is reduced [33].

All these observations date back to the time when the neurosecretory processes in the diencephalon, and their relation to the posterior lobe of the pituitary, were not understood. The results were then explained by the assumption that the control of the neurohypophysis occurred only through nervous impulses, which depend upon the experimental or pathological conditions; the relevant factor was believed to be either a nervous stimulation or inhibition of the activity of the posterior lobe. The basis of this activity was either not known, or was wrongly ascribed to the pituicytes. Today, a different question must be asked: what relationship has the secretory activity of the supraoptico-hypophysial tract, which is represented in all vertebrates, to the retention of water and electrolytes?

If the neurosecretory granules in the posterior lobe of the pituitary represent the carrier substance of the antidiuretic hormone—that is, of vasopressin—one would expect the amount of neurosecretory material, or its staining reaction, to alter when the conditions of water retention are changed. In fact, in amphibia that have been exposed to dehydrating conditions and in mammals suffering thirst, the neurosecretory content of the posterior lobe is considerably reduced [26, 31, 45] (figure 11). One can regard this reduction as a release of antidiuretic hormone, which would decrease the water output of the kidney. Studies [17] with the electron microscope suggest that the loss of specifically staining neurosecretion in the posterior lobe corresponds to an emptying of the granules that have previously been described: the granules take on the appearance of vesicles. Relationships between lactation, which is stimulated by oxytocin, and the neurosecretory content of the posterior lobe can equally well be seen in histological material. Within 24 hours of parturition there is a considerable reduction in the neurosecretory store of the neurohypophysis of the rat [45].

All these observations are in good agreement with the working hypothesis that both the antidiuretic hormone and oxytocin have a neurosecretory origin. The results of extraction experiments on the brain and neurohypophysis of the dog [22, 11] are even more definite. They give information not only about the antidiuretic activity of the system, which has been primarily considered so far, but also about its action upon the blood pressure and about the action of oxytocin upon the uterus and the mammary glands.

It is possible to isolate the parts of the hypothalamus that contain neurosecretion and to test them, qualitatively and quantitatively, for hormone content; a comparison with other parts of the brain can then be made. Such tests (figure 14) show that the neurosecretory nuclear areas,

the pathway between the nuclei and the posterior lobe, and the posterior lobe itself contain vasopressin and oxytocin [22, 11]: regions adjacent to the neurosecretory nuclei are free of these substances. With extracts of the supraoptic and paraventricular nuclei, of the stalk region, and of the posterior lobe of the hypophysis, one can produce a reduction in urine flow with simultaneous concentration of chloride, rise in blood pressure, and contraction of the myo-epithelial cells of the mammary gland and of the smooth muscles of the uterus. The observations that the neurohypophyses of newborn and young animals are very much poorer in posterior-lobe hormones than are those of the adult [19, 20], and also show very much less stainable neurosecretion, are consistent with these findings. Further, the nerve cells of the supraoptic and paraventricular nuclei are not matured—that is, they show no secretory activity.

Demonstration that the secretory neurons of the diencephalon produce definite hormones (one should speak of hypothalamic hormones and not of posterior-lobe hormones [4]) does not exclude the possibility of an influence upon the system transmitted by nervous impulses in the classical neurophysiological sense. In fact, it has also been shown, to mention only one example, that electrical stimulation of a 'drinking-area' in the hypothalamus of the goat leads not only to immediate drinking, but also produces a concurrent antidiuresis and milk release [2]. Electrical stimulation of the area of the supraoptico-hypophysial tract produces only a reduction in water output and a release of milk: it does not lead to drinking.

As noted at the beginning of this article, the structures of vasopressin and oxytocin are known.

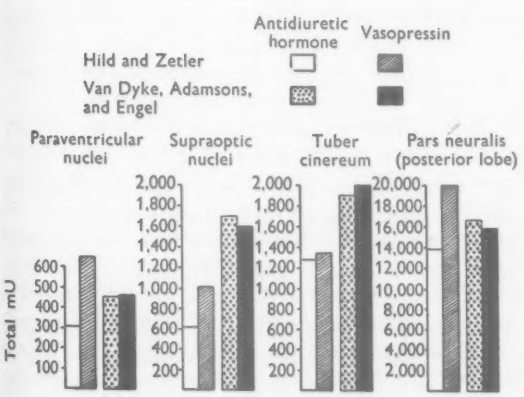


FIGURE 14 – *Results of testing the neurosecretory hypothalamo-hypophysial system for its content of vasopressin and oxytocin* [11].

But what is the significance of the granules that electron microscopy reveals in the secretory cells? Are we dealing with granules that consist of active peptides, are they the hormones themselves, or are they carriers of the hormones?

R. Acher's chemical investigations show [1] that in the posterior lobe there is, besides the biologically active substances, an inactive protein (neurophysin) that appears to be bound to the hormones. This protein is possibly identical with the neurosecretion identifiable under the microscope by its specific staining reaction. The neurosecretion consists of the granules revealed by electron microscopy, but at present it is not known what part of the granules corresponds to neurophysin.

The results of light- and electron-microscopy, and of pharmacological and chemical investigations, give a fairly complete picture of the mode of action of a central neuronal system that is humorally active. This is the only such system that has been morphologically recognized in vertebrates. Our insight into the functional relationship of the hypothalamo-hypophyseal system to the various parts of the anterior lobe is only meagre, even though the two lobes are spatially in the closest relationship. It has been shown that although some neurosecretory fibres may enter the pars tuberalis, they go mainly into the intermediate lobe, where they lie in close contact with the epithelial cells (figure 13). In the hypophyses of fishes the course of the neurosecretory fibres is particularly closely related to the adenohypophysis. Further, nerve fibres that contain neurosecretion reach the capillaries in the hypophysial stalk [4, 39], so that materials from the neurosecretory system could be carried by the portal vessels of the hypothalamo-hypophysial system to the anterior lobe [15, 16].

These morphological findings must be considered together with other observations. For example, the toad sheds its skin under the influence of lysin-vasopressin, provided the anterior lobe of the hypophysis is present [24]. Parenterally administered synthetic vasopressin produces the release of adrenocorticotrophic hormone [ACTH] from the anterior lobe of the rat [29]. In the guinea-pig, an increase in ACTH output can be demonstrated by the raised corticosteroid output in the urine after administration of pitressin, the hormone of the posterior lobe; this effect is not found in animals from which the pituitary has been removed [43]. Further, R. Guillemin, M. Saffran, Schally, and their co-workers [13, 16,

37] have shown, in vitro, a rise in ACTH output under the influence of extracts of the posterior lobe and the hypothalamus. The active substance appears, according to chromatographic analysis, to be a peptide and not identical with either the antidiuretic hormone or oxytocin, nor with acetylcholine, adrenalin, noradrenalin, serotonin, or histamine. However, the peptide does contain a number of amino acids that are also found in vasopressin. The possibility cannot be excluded that the neurosecretory system of the diencephalon influences the activity of the anterior lobe [15, 28]. The unequivocal demonstration of such an influence would throw light on the mystery of the intimate relationship between the diencephalon (and the posterior lobe) and the epithelial part of the hypophysis.

The members of the system that control internal secretion are interrelated. An effector organ acts as a regulator only when information from the target organ reaches it through neural or humoral paths [9]; only under these circumstances can it act in a purposeful way. This mutual interplay can be studied even in the case of the neurosecretory hypothalamo-hypophysial system. Thus the mechanical stimulation of the nipple in suckling or milking leads to an excitation which reaches the central nervous system by a neural path and causes release of oxytocin. The oxytocin is carried by the blood to the mammary gland. There it produces contraction of muscle cells around the alveoli and thus the expression of milk (see figure 15). The cessation of the mechanical stimulus diminishes the release of oxytocin.

Research into such interrelationships is only just beginning. Recently a connection has been suggested between the hypothalamo-hypophysial system and the visual apparatus. For example, disturbances in water retention have been found in blind people. Further, it is known that light can stimulate sexual activity in birds and mammals [48, 7, 8], and this probably occurs through the hypothalamus and the epithelial portion of the hypophysis. It is thought that the anterior lobe is stimulated by hypothalamic substances, reaching it through the blood stream. Recent careful investigations of the neurosecretory system of a North American finch *Zonotrichia leucophrys gambelii* support such a view. They showed clear quantitative differences in the amount of neurosecretion in the neurosecretory cells of the diencephalon and in their efferent tracts during the course of a year, that is, in relation to the gonadal development and the intensity and duration of

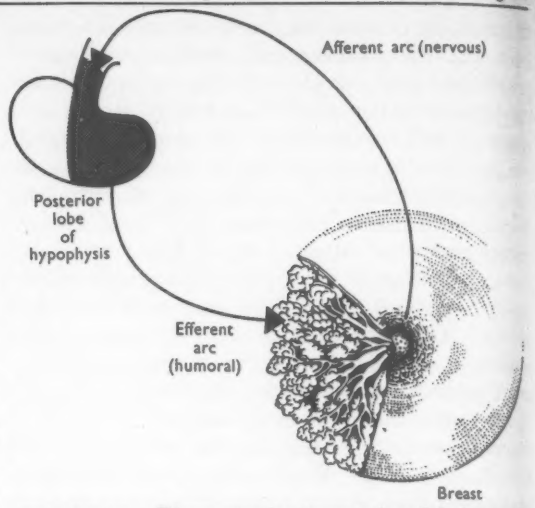


FIGURE 15 – *Diagrammatic representation of the interaction between the mammary gland and the neuro-hypophysis* [9].

light [30]. Further, it has been possible experimentally to reduce the neurosecretory material in the region of the nuclei and in the tuber cinereum by lengthening the daily exposure to light. At the same time there was an increase in testicular and body weight.

When one considers these phenomena, which it is not possible to describe fully here, the questions arise whether the diencephalic hormones that act upon the anterior lobe are identical with, or similar to, vasopressin and oxytocin, and whether regions other than the neurosecretory-cell areas control the gonadotropic activity of the pituitary [44]. We shall gain a complete understanding of the complex regulatory system only when we survey the relationships between the diencephalon, the pituitary, and the other endocrine organs. This applies also to what happens in the metamorphosis of lower animals, such as the brook lamprey, during which the neurohypophysial neurosecretion, previously abundant, disappears [25].

It is still not clear how the hypothalamic hormones stored in the terminal parts of the neurosecretory pathway are released into the capillaries in the stalk region and in the region of the posterior lobe itself. Only rarely has neurosecretion been found in the vascular lumen. The conversion of the electron-microscopical granules of neurosecretion into vesicles, previously described, could be equivalent to a release process. Perhaps further analysis of this process is not possible by morphological means.

With the discovery of the humoral activity of certain diencephalic neurons, the organization of

the central mechanism for controlling vegetative processes appears in a new light. A central-nervous portion of the autonomic system can also function as an endocrine gland, the diencephalic gland, which acts not only upon distant organs, but apparently upon the adjacent anterior lobe, by humoral paths. Clearly the endocrine and central-nervous autonomic systems act together in the coordination and maintenance of the vegetative functions of the organism.

REFERENCES

[1] ACHER, R. In 'II. International Symposium on Neurosecretion, Lund, 1957', pp. 71–78. Springer-Verlag, Berlin. 1958.

[2] ANDERSSON, B. and MCCANN, S. M. *J. Physiol.*, **129**, 44, 1955.

[3] BARGMANN, W. *Z. Zellforsch.*, **34**, 610, 1949.

[4] *Idem.* 'Das Zwischenhirn-Hypophysensystem'. Springer-Verlag, Berlin. 1954; *Proc. 8th Symp. Colst. Res. Soc. Bristol*, **8**, 11, 1957.

[5] *Idem.* In 'II. International Symposium on Neurosecretion, Lund, 1957', pp. 4–12. Springer-Verlag, Berlin. 1958.

[6] BARGMANN, W. and SCHARRER, E. *Amer. Scient.*, **39**, 255, 1951.

[7] BENOIT, J. *Rev. suisse Zool.*, **65**, 577, 1957.

[8] BENOIT, J. and ASSENMACHER, I. *J. Physiol.*, **427**, 237, 1955.

[9] BERDE, B. 'Recent Progress in Oxytocin Research'. American Lecture Ser. No. 360. Springfield, Illinois. 1959.

[10] CARLISLE, D. B. In 'II. International Symposium on Neurosecretion, Lund, 1957', pp. 18–19. Springer-Verlag, Berlin. 1958.

[11] VAN DYKE, H. B., ADAMSONS, K., jr, and ENGEL, S. L. *Recent Progr. Hormone Res.*, **11**, 1, 1955.

[12] GAUPP, R., jr. *Klin. Wschr.*, 1012, 1934; *Fortschr. Neur. Pschiat.*, **13**, 257, 1941.

[13] GUILLEMIN, R. *Endokrinologie*, **34**, 193, 1957.

[14] HANSTRÖM, B. *Nature, Lond.*, **171**, 72, 1953.

[15] HARRIS, G. W. 'Neural control of the pituitary gland'. Edward Arnold (Publishers) Ltd, London. 1955.

[16] FIELDS, W. S., GUILLEMIN, R., and CARTON, C. A. (Editors). In 'Hypothalamic-hypophysial interrelationships. A symposium'. Springfield, Illinois. 1956.

[17] HARTMANN, J. F. *Z. Zellforsch.*, **48**, 291, 1958.

[18] HELLER, H. *Experientia*, **6**, 368, 1950.

[19] HELLER, H. and LEDERIS, K. *J. Physiol.*, **147**, 299, 1959.

[20] HELLER, H. and ZAIMIS, E. J. *Ibid.*, **109**, 162, 1949.

[21] HILD, W. *Acta neuroveg.*, **3**, 81, 1951; *Z. Zellforsch.*, **40**, 257, 1954.

[22] HILD, W. and ZETLER, G. *Experientia*, **7**, 189, 1951; *Arch. exp. Path. Pharmak.*, **213**, 139, 1951; *Pflüg. Arch. Ges. Physiol.*, **257**, 169, 1953; *Z. exp. Med.*, **120**, 236, 1953.

[23] HINSEY, J. C. and MARKEE, J. E. *Amer. J. Physiol.*, **106**, 48, 1953.

[24] JØRGENSEN, C. B. and OLESEN LARSEN, L. *Ergebn. Biol.*, **22**, 1, 1960.

[25] VAN DE KAMER, J. C. and SCHREURS, A. F. *Z. Zellforsch.*, **49**, 605, 1959.

[26] KRATZSCH, E. *Ibid.*, **36**, 371, 1951.

[27] MARKEE, J. E., EVERETT, J. W., and SAWYER, C. H. *Recent Progr. Hormone Res.*, **7**, 139, 1952.

[28] MARTINI, L., MIRA, L., PECILE, A., and SAITO, S. *J. Endocrin.*, **18**, 245. 1959.

[29] MCCANN, S. M. *Endocrinology*, **60**, 664, 1957.

[30] OKSCHE, A., LAWS, D. F., KAMEMOTO, F. J., and FARNER, D. S. *Z. Zellforsch.*, **51**, 1, 1959.

[31] ORTMANN, R. *Ibid.*, **36**, 92, 1951.

[32] PALAY, S. L. *Anat. Rec.*, **121**, 384 (Abstract No. 247), 1955; *Progr. Neurobiol.*, Vol. II, 'Ultrastructure and Cellular Chemistry of Neural Tissue', pp. 31–49, 1957.

[33] PICKFORD, M. *J. Physiol.*, **106**, 264, 1947.

[34] RANSON, S. W., FISHER, C., and INGRAM, W. R. *Res. Publ. Ass. nerv. ment. Dis.*, **17**, 410, 1938; *Amer. J. Physiol.*, **109**, 57, 1934; *Endocrinology*, **23**, 175, 1938.

[35] RANSON, S. W. and MAGOUN, H. W. *Ergebn. Physiol.*, **41**, 56, 1939.

[36] RODECK, H. Supplement to *Arch. Kinderheilk.*, No. 36. F. Enke Verlag, Stuttgart. 1958.

[37] SAFFRAN, M., SCHALLY, SEGAL, and ZIMMERMANN. In 'II. International Symposium on Neurosecretion, Lund, 1957', pp. 55–59. Springer-Verlag, Berlin. 1958.

[38] SANO, Y. and HARTMANN, F. *Z. Zellforsch.*, **48**, 538, 1958.

[39] SCHARRER, B. and SCHARRER, E. 'Neurosekretion'. In 'Handbuch der mikroskopischen Anatomie des Menschen', Vol. VI. Springer-Verlag, Berlin. 1954.

[40] SCHARRER, E. and WITTENSTEIN, G. J. *Anat. Rec.*, **112**, 387, 1952.

[41] SCHIEBLER, T. H. *Naturwissenschaften*, **45**, 214, 1958.

[42] SLOPER, J. C. *Nature, Lond.*, **179**, 148, 1957; *Internat. Rev. Cytol.*, **7**, 337, 1958.

[43] SOBEL, H., LEVEY, R. S., MARMORSTON, J., SCHAPIRO, S., and ROSENFELD, S. *Proc. Soc. exp. Biol., N.Y.*, **89**, 10, 1955.

[44] SPATZ, H. 'Zentrale Steuerung der Sexualfunktionen'. In 'I. Symposium Deutsche Gesellschaft für Endokrinologie, 1953'. Springer-Verlag, Berlin. 1955.

[45] STUTINSKY, F. *Ann. Endocr.*, **14**, 722, 1953.

[46] *Idem. Bull. microsc. Appl., Mém. hors série*, **2**, 1, 1957.

[47] VERNEY, E. B. *Proc. roy. Soc., B*, **135**, 27, 1947; *Brit. med. J.*, 119, 1948.

[48] ZUCKERMAN, S. *J. Méd., Bordeaux*, **135**, 121, 1958.

Phosphonitrilic derivatives

N. L. PADDOCK

Many of the properties of the phosphonitrilic compounds suggest that they will find uses as heat-resistant polymers. The compounds show a number of features commonly met in organic chemistry, including a form of aromatic character and various types of isomerism. Research has demonstrated some of the new factors which must be taken into account when phosphorus is involved in a polymeric system. This article describes some of the recent theoretical and practical advances in this growing branch of inorganic chemistry.

Phosphonitrilic derivatives are a series of chemical compounds containing the repeating unit $-\overset{|}{\underset{|}{P}}=N-$, and interest in them is growing rapidly in many parts of the world [1]. There are many reasons for this. Much of the work has been inspired by the high thermal stability of some of the compounds, which has encouraged the hope that they may be made the basis of materials with useful properties at high temperatures. Such materials may include fluids with uses in hydraulics, heat transfer, and lubrication, as well as solids with the mechanical properties of familiar organic polymers. The recent recognition of phosphonitrilic compounds as 'aromatic' systems has stimulated research because, in the organic field, aromatic compounds are distinguished by their chemical and thermal stability; it is therefore reasonable to look for similar properties in an inorganic aromatic series.

There is, however, much to be done before the full practical benefit of this research is obtained. The effort to obtain useful high-temperature polymers had led to the accumulation of a large number of experimental facts, which are now being unified in terms of structural and theoretical principles. In this way the subject is acquiring another sort of importance, and it is now one of the important growing-points of inorganic chemistry.

The development of modern organic chemistry, particularly in its physical aspects, has depended in part on the stability of the fundamental carbon skeleton, which allows varied substitution so that a study of the effect of substitution on reaction rates and mechanism can be made. In this way an intimate understanding of reactions at carbon centres has been obtained. In inorganic chemistry, on the other hand, stable homologous series are rare. It can be expected, therefore, that detailed investigation of the exceptional phosphonitrilic series, in which the substituents can be varied widely without disruption of the P—N skeleton, will provide a further insight into the chemistry of phosphorus. The purpose of the present article is to set the phosphonitrilics in their chemical context, and to suggest where the next advances are most likely to be made.

PREPARATION

There are two main ways of preparing phosphonitrilic derivatives. The first depends on the ammonolysis of a suitable compound of pentavalent phosphorus, and is exemplified by the procedure used by H. N. Stokes and developed by R. Schenk and G. Römer [2]. Phosphorus pentachloride is heated with ammonium chloride in a refluxing inert solvent; the reaction proceeds smoothly and almost quantitatively

$$PCl_5 + NH_4Cl \longrightarrow \frac{1}{n}(PNCl_2)_n + 4HCl$$

and if conditions are properly chosen, the product is composed almost wholly of cyclic polymers. The trimer is the most abundant, the yields of higher polymers decreasing slowly with increasing degree of polymerization. Stokes isolated the individual polymers up to the heptamer, and was left with an undistillable oil of the same empirical composition, which he believed to contain still higher cyclic polymers [3]. Recent work has substantiated his belief. Other derivatives can be prepared in a similar way, for instance the phenyls $(PNPh_2)_{3,4}$ from Ph_3PCl_3 [4], the methyls $(PNMe_2)_{3,4}$ [5], the bromides [6], and a number of mixed derivatives. The other preparative method depends on substitution reactions of an existing phosphonitrilic compound, which is usually one of the comparatively readily available chlorides. The fluorides, alkoxides, alkylamides, and many other series of compounds have been obtained in this way. Many examples of phosphonitrilic derivatives

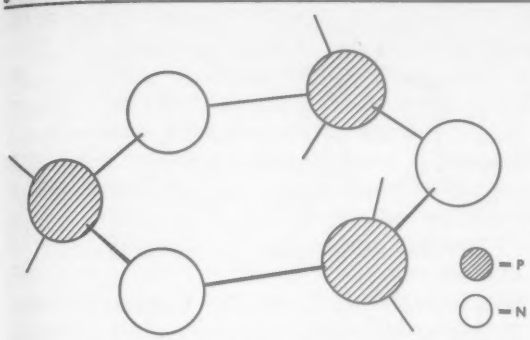
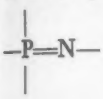


FIGURE 1 – *The structure of the triphosphonitrilic chloride molecule. The chlorine atoms are not shown.*

prepared by one of these two routes will be referred to below; they are all formed from repeating



–P=N– units.

TRIMERIC COMPOUNDS

The most familiar of the phosphonitrilics is the trimeric chloride $(PNCl_2)_3$, which is often written as if it contained three double bonds. In fact, the ring bonds are all equal within experimental error [7], their length being close to 1·60Å, compared with the value of 1·78 Å found for the single P—N bond in the phosphoramidate ion $NH_2PO_3^{2-}$ [8]. The molecule has the structure shown in figure 1. It is nearly flat in the crystal; the small deviations from planarity that do occur probably result from mutual repulsion of chlorine atoms in adjacent molecules. Spectroscopic results also require the ring bonds to be equal and the ring to be flat [9]. Structurally, the trimeric chloride resembles benzene. Chemically, it is less reactive than most phosphorus-chlorine compounds: complete replacement of the chlorine atoms by amino groups is possible, for instance, but the reaction requires extreme conditions [10]. Some of the compounds obtained by substitution reactions are shown in figure 2. The methoxy compound is soluble in water [11], and easily eliminates dimethyl ether between molecules; the isothiocyanate polymerizes very readily [12], though whether this occurs by opening of the ring or through the NCS group is not yet known. The chloride undergoes the Friedel-Crafts reaction with benzene, a diphenyl derivative being formed [13]; the fluoride $P_3N_3F_6$ is prepared from the chloride and potassium fluorosulphite [14]. The hydrazide $P_3N_3(NH.NH_2)_6$ has been recently prepared [15], and undergoes further reactions typical of the attached groups.

These derivatives, and similar ones, exhibit a wide range of chemical and physical behaviour. They include such different compounds as the fluoride, which melts just above room temperature and boils at 51°, and the methyl derivative $P_3N_3Me_6$, which melts at 195°; the first is insoluble in polar liquids, even in concentrated sulphuric acid, the second dissolves easily in water. All the derivatives have in common a cyclic P_3N_3 nucleus, in which the bond strength depends on the electronegativity of the attached groups. This is shown qualitatively in figure 3, in which the frequency of the E^1 ring vibration is plotted against the Pauling electronegativity of the atom attached to the phosphonitrilic ring. The observed frequency, which can be seen to increase with the electronegativity of the ligands, may be taken as an approximate measure of the stretching constant of the P—N bond, and hence of its strength, which is thus shown to be greatest in the fluoride.

Partially substituted derivatives are also known. Some, such as the chlorobromides, are formed from mixed phosphorus halides [16], but most of them are prepared by substitution

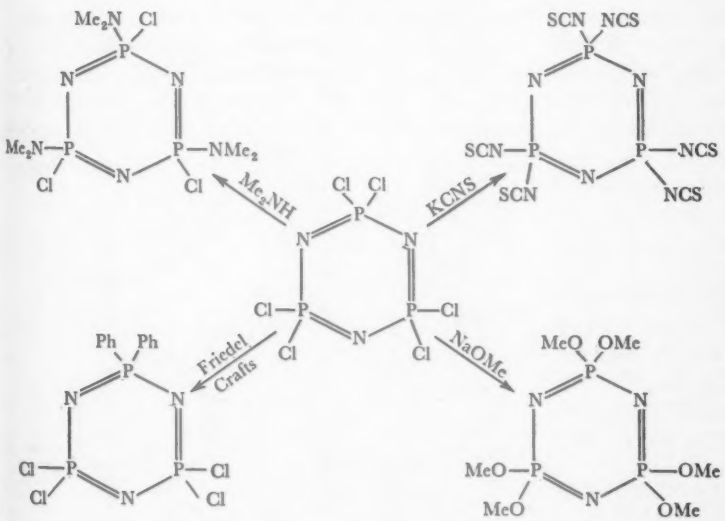


FIGURE 2 – *Some reactions of triphosphonitrilic chloride.*

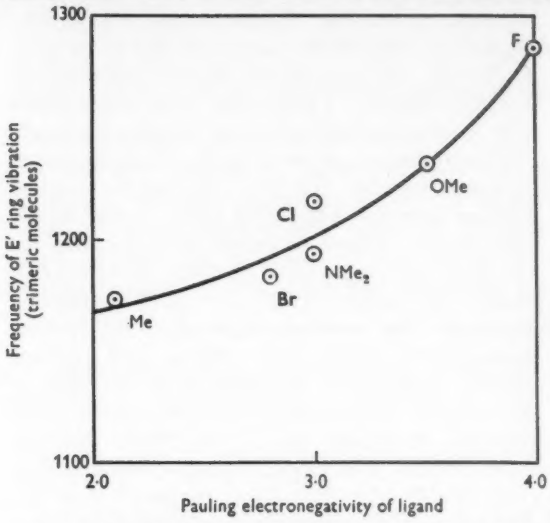


FIGURE 3 – *The effect of ligand electronegativity on ring-vibration frequency.*

reactions. In many cases, such as partial hydrolysis or the Friedel-Crafts reaction, it is usual for the product to contain an even number of each type of group. It was naturally supposed that substitution occurs pairwise on each phosphorus atom, and this has indeed been shown, by degradation experiments, to be so for the diphenyl compound [13]. For compounds with an odd number of substituents this clearly cannot be true, and the dimethylamino derivative $P_3N_3Cl_3(NMe_2)_3$ has in fact been shown to be symmetrically substituted [17]. It is also certain that in some di-derivatives the substituents are attached to different phosphorus atoms, and the concept of pairwise substitution is therefore an oversimplification.

We are thus led to the possibility of isomerism in mixed derivatives, and a number of laboratories are actively engaged in studying this field. Since no change takes place at the nitrogen atoms, the geometrical problem is the same as for cyclopropane. Chemically, the interest lies in the fact that the orientational effects on a second substituent will be derived not only from the ring, as in benzene, but also from the first substituent. From more complete studies than have yet been made it will be possible to assess the effectiveness of this type of aromatic nucleus in relaying chemical influences and the relative importance of steric and electronic effects.

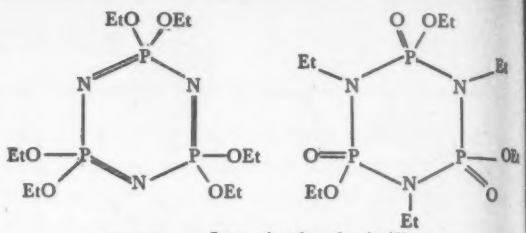


FIGURE 4 – *Isomeric phosphonitrilic esters.*

Other types of isomerism are found. The trimeric chloride may be hydrolysed to the corresponding acid, in which the replacement of the chlorine atoms by hydroxyl groups is followed by a tautomeric change:

$$—P(OH)_2{=}N— \rightarrow —PO(OH)—NH—$$

This type of keto-enol tautomerism is similar to that found in cyanurates, which have a C_2N_3 nucleus, and in both cases N-chloro compounds can be prepared from the salts [18]. Structural isomerism of a related type is also known: R. Rätz and M. Hess [19] obtained the normal ethyl ester by alcoholysis of the chloride, and the N-ethyl ester by treatment of the silver salt of triphosphonitrilic acid with ethyl iodide. Both forms are shown in figure 4.

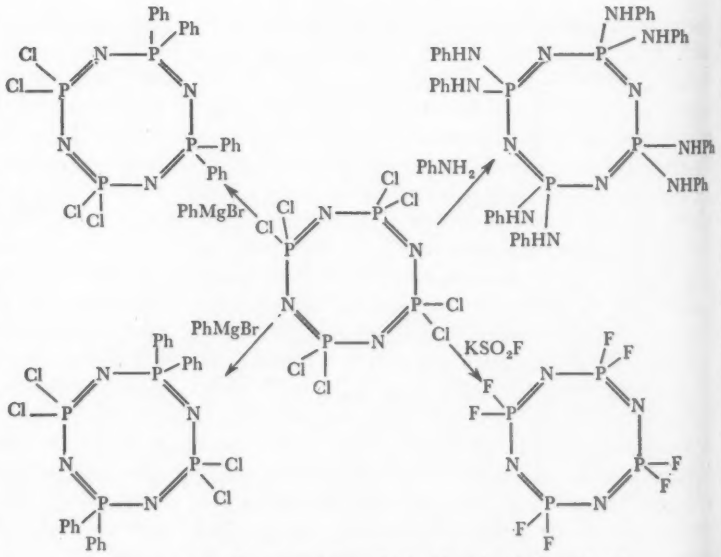


FIGURE 5 – *Some reactions of tetraphosphonitrilic chloride.*

TETRAMERIC COMPOUNDS

Treatment of the trimeric chloride with lead fluoride gives a mixture of tetrameric chlorofluorides, the only reaction so far reported in this series in which alteration in ring-size occurs [20]. Otherwise, trimeric and tetrameric compounds are obtained in similar ways. Figure 5 shows some of the substitution reactions of the tetrameric chloride. The anilide is very readily prepared, the NH groups being available for further reaction; as with the trimer, the fluoride may also be easily obtained [14]. Tetraphosphonitrilic acid, prepared by hydrolysis of the chloride, is very stable, and, like its trimeric analogue, appears to exist principally in the imido form. Infra-red studies on its dihydrate show, however, that intermolecular hydrogen-bonding is an important feature of the crystal, and the distinction between the two tautomeric forms is not as great as may appear [21]. Structural isomerism of the ethyl esters also occurs, just as with the trimeric compounds.

The tetrameric chloride reacts with phenylmagnesium bromide to give not only the fully phenylated derivative $P_4N_4Ph_8$, but also two tetraphenyl phosphonitriles [22], which are probably the position isomers shown in figure 6. In two other tetraphenyl-tetrachloro compounds, recently prepared by the ammonolysis of $PhPCl_4$ [23], it is likely that each phosphorus atom carries one phenyl group, so that the compounds must be two out of the four possible stereoisomers shown in figure 6.

Although the ring is shown here in a planar form, at least two different configurations have been found experimentally: they are illustrated in figure 7. The boat form is found in the chloride [24] and the chair form in the fluoride. Two forms of the fully phenylated derivative have

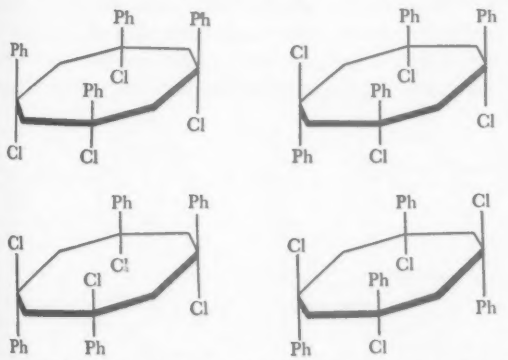


FIGURE 6 – *Stereoisomers of the tetrameric compound* $(PNPhCl)_4$.

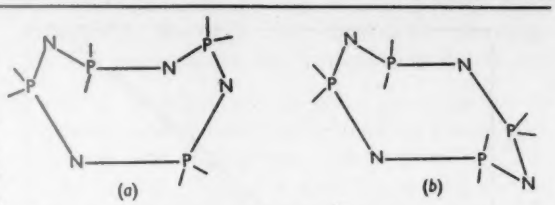


FIGURE 7 – *The skeletal structures of* (a) *tetraphosphonitrilic chloride,* (b) *tetraphosphonitrilic fluoride.*

been reported [22], and it is possible that this compound may exist in both configurations, interconversion being hindered by the bulky phenyl groups. The possibilities open to an eight-membered ring are, however, more numerous than the simple boat and chair forms characteristic of six-membered rings; for instance, a number of different symmetries have been found experimentally for the tetrametaphosphate ion $(-PO_2-O-)_4^{4-}$ in different environments [25].

Such configurational isomerism would increase the number of isomers considerably, and if either of the forms shown in figure 7 were rigid, two *cis*-1 : 2 derivatives would be obtainable. In practice it is most likely that barriers to internal motion are small and that, for chemical purposes, representation as a planar ring is adequate. The isomers obtained are therefore analogous in structure to those of cyclobutane derivatives.

Although they have not yet been explored in such detail, the chemical properties of the tetrameric compounds resemble closely those of compounds based on the six-membered ring. At first sight this is surprising, because cyclo-octatetraene, the corresponding compound in the carbon series, is a typical unsaturated substance and has no aromatic properties. Since the skeletal structure of tetraphosphonitrilic chloride is so closely similar to that of cyclo-octatetraene (figure 7*a*), one might expect in the phosphonitrilic series, too, a greater difference between the six-membered and eight-membered rings. The bonds in the phosphonitrilic compound are, however, all equal in length [24], whereas in cyclo-octatetraene they alternate between single and double bonds [26]. Some new structural feature is evidently involved, which allows retention of the characteristic properties of the trimeric compounds in larger rings in a way which is not possible in the carbocyclic series.

HIGHER POLYMERS

The existence of aromatic properties in eight-membered and larger rings is the key point of

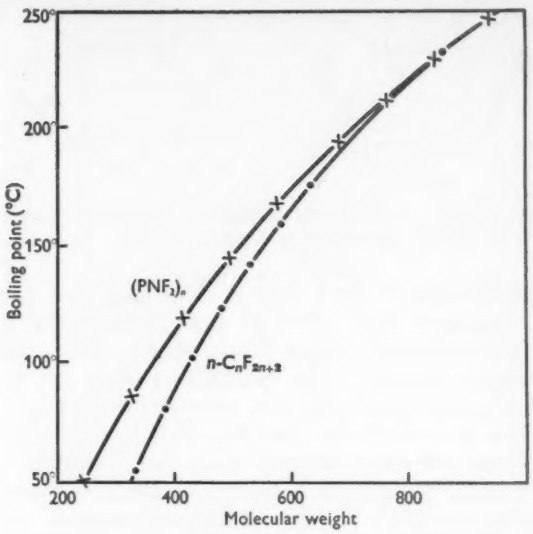


FIGURE 8 – *The boiling-points of the phosphonitrilic fluorides* $(PNF_2)_n$ *compared with those of the n-fluorocarbons* [36].

difference between the phosphonitrilics and their organic analogues. Stokes isolated three further members of the chloride series [3] and, from a mixture of higher chlorides similar to the undistillable residue already referred to, fluorides up to $(PNF_2)_{17}$ have now been obtained [27]. Both chlorides and fluorides polymerize to a rubbery solid on heating to 350°.

No account of work on the reaction of these higher polymers has yet been published, but it is known that the higher chlorides are not much more reactive to nucleophilic reagents such as the hydroxide ion than are the trimer and tetramer. Their nuclear magnetic resonance spectra show them to be all monocyclic, and the infra-red spectra of the fluorides show that the stretching constant of the P—N bond undergoes only small and smooth variation as the series is ascended. Although there is no detailed evidence, such as bond lengths and angles, about the structure of the pentameric and larger molecules, both chemical and physical investigations show that the higher polymers are, structurally, larger rings of essentially the same character as that of the trimer and tetramer.

The principal difference is that molecular flexibility becomes more obvious; this can be seen particularly clearly in the physical properties of the fluorides [27]. In many of their properties they resemble the *n*-paraffinic fluorocarbons, in particular in their boiling-points. These are plotted in figure 8 as a function of molecular weight for both series. The intermolecular forces are therefore comparably low. The viscosity behaviour of the two series is nevertheless quite different, because, with the larger molecules, transfer of momentum is increasingly dependent on freedom of movement within the molecule. The work of C. W. Bunn on polytetrafluoroethylene [28] has shown that the carbon skeleton in this molecule is sheathed with closely packed fluorine atoms. In small fluorocarbons, too, a similar packing must make the whole molecule rigid, and molecular motion takes place in large segments. The activation energy for viscous flow in the fluorocarbons is therefore a large fraction of the energy of vaporization. The phosphonitrilic fluorides, on the other hand, are much less crowded molecules, and the interaction of fluorine atoms on different phosphorus atoms is small. Accordingly, the viscosities of the phosphonitrilic fluorides are low (the pentamer and water have about the same viscosity, measured at 20° C), and, because of the high flexibility, the energy of activation for viscous flow (equivalent to the temperature coefficient of viscosity) is also small. They are, in fact, lower than for the corresponding dimethylsiloxanes—outstanding themselves in this respect—as may be seen by comparing corresponding activation energies: 2·54 kcal per mole for $(PNF_2)_5$, 3·42 kcal per mole for $(Me_2SiO)_5$.

CHEMICAL BINDING IN THE PHOSPHONITRILIC SERIES

We have seen that the phosphonitrilics are characterized by a ring system whose structural and chemical properties suggest aromatic character. This is displayed in a wider range of ring sizes than is possible in carbocyclic systems, and is associated with a high flexibility.

Tervalent phosphorus does not normally form multiple bonds, and is not often found as part of an unsaturated system. While the nitrogen molecule, N_2, is triply bonded, the phosphorus

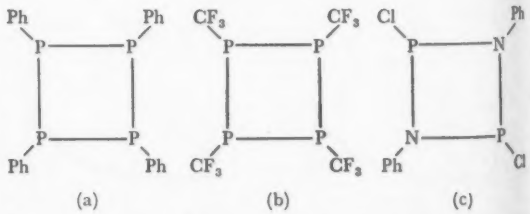


FIGURE 9 – *Phosphorus compounds containing four-membered rings.*

molecule, P_4, is tetrahedral, each atom being joined to the other three by single bonds. Again, the double bond between the nitrogen atoms in azobenzene is sufficiently well defined to permit the stable existence of geometrical isomers. The phosphorus analogue, on the other hand, is dimeric, and presumably has the four-membered-ring structure shown in figure 9*a*. The trifluoromethyl derivatives recently described by A. B. Burg [29] are also polymeric; the tetramer $(CF_3P)_4$ (figure 9*b*) and the pentamer $(CF_3P)_5$ have also been described. In the phosphorus-nitrogen series, too, a four-membered ring has been shown to exist [30] in the compound $(PhN{:}PCl)_2$; the molecule does not, therefore, contain a true double bond (figure 9*c*).

A normal double bond, such as that between carbon and oxygen, is formed by overlap between two orbitals of cylindrical symmetry along the direction of the bond (σ-bond) and between two 2p-orbitals perpendicular to the bond direction (π-bond). The formation of a π-bond in this way is illustrated in figure 10*a*; the σ-bond is omitted for clarity. The shapes indicate regions of high electron-density, and overlap between regions of the same sign corresponds to an increased density, and hence formation of a covalent bond. The 3p-orbital of a phosphorus atom, on the other hand, does not form an effective π-bond, because it is too directional, too well shielded, and too far from the adjacent atom.

In derivatives of pentavalent phosphorus, however, all the 3p-orbitals are used in forming four hybridized bonds, and 3d-orbitals become available for bonding. The overlap scheme for a phosphoryl bond (for example in $POCl_3$) is shown in figure 10*b* [31]. A π-bond of this type is possible because overlap takes place well away from the nucleus and is not too sensitive to internuclear separation. As a result of the different shapes of the two orbitals concerned, the region of highest electron density is much closer to the oxygen than to the phosphorus atom, so automatically

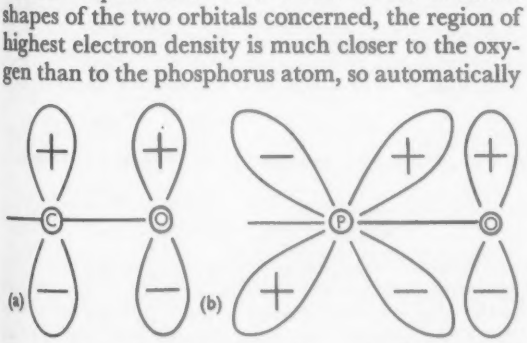


FIGURE 10 – *The formation of a π-bond in* (a) *the carbonyl group,* (b) *the phosphoryl group.*

introducing an appreciable polarity. The distinction between the two formulations P=O and $\overset{+}{P}—\overset{-}{O}$ is therefore not as great as is commonly supposed, and the high polarity of the phosphoryl group is not inconsistent with a pure covalent double bond. Its great strength is the driving force behind the easy isomerization

$$P(OMe)_3 \longrightarrow MePO(OMe)_2$$

and many other similar reactions.

Just as the existence of localized π-bonds in ethylene and in carbonyl compounds leads naturally to the recognition of a delocalized system of bonds in benzene, so the concept of d—p overlap described above can also be extended to delocalized systems, and is probably exemplified in the series of cyclic phosphonitrilic compounds [32].

The different symmetries of d- and p-orbitals, however, introduce a new feature: the p-orbital changes sign on inversion through its centre, whereas the d-orbital does not. This has the effect of inverting the molecular energy levels, and as a result, the topmost occupied orbital in the ring compounds is non-degenerate, provided that the electronegativities of the two types of ring atom are different. Closed electronic shells are therefore formed by any even number of π-electrons, and the structural features and chemical inactivity associated with benzene are found, not only in trimeric phosphonitrilic derivatives, but also in the eight-membered and larger rings [32].

The origin of this effect may be seen by reference to figure 11, which shows overlap schemes for p—p and d—p π-bonding. In figure 11*a* the signs of all the p-orbitals are matched, and delocalization is complete; the diagram therefore corresponds to the lowest level of benzene, in which the π-electrons move in the largest possible volume, and in which their kinetic energy is therefore least. In figure 11*b* all the d-orbitals and all the p-orbitals are again taken to be of the same sign, but their different inversion properties introduces one node of zero electron-density for each PN group. The electrons in this molecular orbital are therefore comparatively confined, and have a high energy. In figures 11*c* and 11*d* the orbital signs are arranged to alternate in pairs. This allows perfect matching of the d—p-orbitals, and this arrangement therefore corresponds to the lowest energy. For the same arrangement of signs, nodes appear in the p—p overlap scheme, with conequent increase of energy over that shown in figure 11*a*. The energy-level schemes for

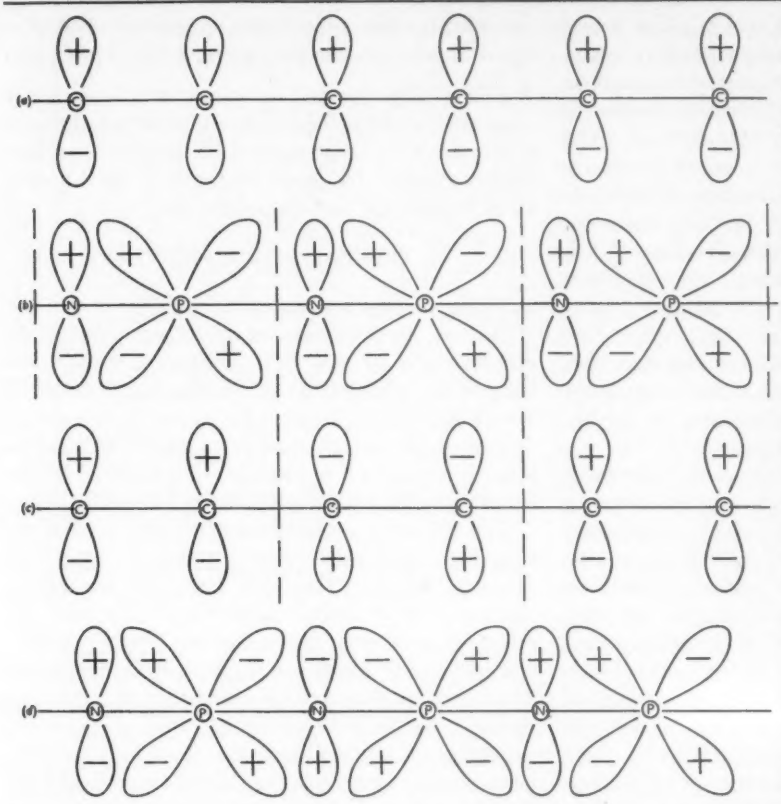


FIGURE 11 – *Overlap schemes for the formation of delocalized π-bonds from p-orbitals* (a *and* c), *and from alternate d- and p-orbitals* (b *and* d). *The dotted lines correspond to interatomic nodes.*

trimeric and tetrameric molecules are shown in figure 12: in neither of these is the highest occupied orbital degenerate. They are to be distinguished from that for cyclo-octatetraene, in which this orbital is degenerate and only half filled, and which has therefore an enhanced chemical reactivity compared with benzene.

FURTHER DEVELOPMENTS

The development of aromatic character of the type described has been shown to be dependent on the electronegativity of the groups attached to the phosphorus [32, 33]; theoretically, π-electron energy should increase with electronegativity, and figure 3 shows that the ring-vibration frequencies do in fact vary in the way expected. It is also to be expected that π-electron energy should increase steadily to a limit with increasing ring size [32]. This quantity cannot be directly measured, and even the total bond energy depends on an arbitrary division of the molecular atomization energy into parts corresponding to P—Cl and P—N bond-energy terms. It does seem, however, that there is some strengthening of the ring in going from trimer to tetramer, as expected.

At first sight the flexibility of the fluorides seems to be rather higher than is appropriate to a π-electron system. The requirement of planarity for this type of aromaticity is not a strict one, because the restrictions on the orientation of the d-orbitals arising from the symmetry of the underlying s- and p-orbitals are only slight, and they can therefore accommodate themselves to give the best overlap with their neighbours; they are also large and comparatively diffuse. Freedom of torsional movement would also be permitted by the wide spacing of the substituent groups; the torsional rigidity of the C—C bonds in hydrocarbons arises from the interaction of the substituents attached to adjacent carbon atoms. Nevertheless, in a more refined theory it may be necessary to include contributions from the other d-orbitals.

From a chemical point of view this inclusion is perhaps even more important, because chemical reactivity depends at least as much on the orbitals which are vacant, and are therefore able

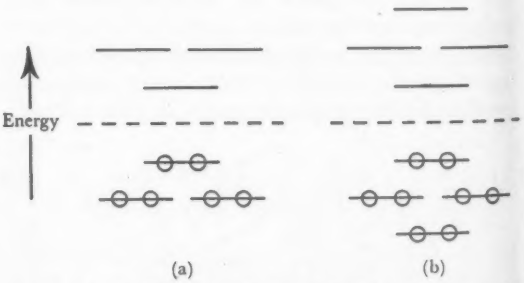


FIGURE 12 – *Energy-level schemes for* (a) *trimeric and* (b) *tetrameric phosphonitrilic molecules. The levels marked with circles correspond to the bonding orbitals. Distances below the dotted line represent stabilization energies with respect to an arbitrary zero. Levels above the line correspond to antibonding orbitals.*

to form bonds with an attacking reagent with electrons to spare, as on those which are already contributing to the bonds. The main features of phosphonitrilic structure and reactions can be understood in terms of the theory described above; the finer details seem most likely to appear, as in organic chemistry, from studies on kinetics and mechanism, particularly those of substitution reactions.

There are also, however, some major general effects still unexplained. Many phosphorus compounds are remarkable in that important structural changes often take place easily; for instance, the isomerization of trimethyl phosphite, referred to above. Similar reactions also take place in the phosphonitrilic series. Replacement of an imido group in the tetraphosphonitrilate ion by an oxygen atom takes place readily [34], and I. I. Bezman [35] has recently found that triphosphonitrilic chloride reacts with sodium benzoate to give benzonitrile and sodium metaphosphate; —P=N—P= is replaced by —P—O—P—. The barriers to the attainment of equilibrium are therefore often low, although the circumstances are not yet understood. The elucidation of such changes, in the phosphonitrilic field and in other parts of the chemistry of phosphorus and the other second-row elements, may well be the next point of advance.

ACKNOWLEDGMENTS

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REFERENCES

[1] General reviews, with fuller references: AUDRIETH, L. F., STEINMAN, R., and TOY, A. D. F. *Chem. Rev.*, **32**, 109, 1943. PADDOCK, N. L. and SEARLE, H. T., in 'Advances in Inorganic Chemistry and Radiochemistry', Vol. 1, Academic Press Inc., New York. 1959.
[2] SCHENK, R. and RÖMER, G. *Ber. dtsch. chem. Ges.*, **57***B*, 1343, 1924.
[3] STOKES, H. N. *Amer. chem. J.*, **19**, 782, 1897.
[4] HABER, C. P., HERRING, D. L., and LAWTON, E. A. *J. Amer. chem. Soc.*, **80**, 2116, 1958.
[5] SEARLE, H. T. *Proc. chem. Soc., Lond.*, 7, 1959.
[6] BODE, H. *Z. anorg. Chem.*, **252**, 113, 1943.
[7] POMPA, F. and RIPAMONTI, A. *Ric. Sci.* **29**, 1516, 1959; WILSON, A. and CARROLL, D. F. *J. chem. Soc.* (In press.)
[8] HOBBS, E., CORBRIDGE, D. E. C., and RAISTRICK, B. *Acta Cryst.*, **6**, 621, 1953.
[9] DAASCH, L. W. *J. Amer. chem. Soc.*, **76**, 3403, 1954.
[10] AUDRIETH, L. F. and SOWERBY, D. B. *Chem. and Ind.*, 748, 1959.
[11] DISHON, B. *J. Amer. chem. Soc.*, **71**, 2251, 1949.
[12] OTTO, R. J. A. and AUDRIETH, L. F. *Ibid.*, **80**, 5894, 1958.
[13] BODE, H. and BACH, H. *Ber. dtsch. chem. Ges.*, **75***B*, 215, 1942.
[14] SEEL, F. and LANGER, J. *Angew. Chem.*, **68**, 461, 1956.
[15] OTTO, R. J. A. and AUDRIETH, L. F. *J. Amer. chem. Soc.*, **80**, 3575, 1958.
[16] RICE, R. G., DAASCH, L. W., HOLDEN, J. R., and KOHN, E. J. *J. inorg. nucl. Chem.*, **5**, 190, 1958.
[17] BECKE-GOEHRING, M., JOHN, K., and FLUCK, E. *Z. anorg. Chem.*, **302**, 103, 1959.
[18] TAYLOR, M. C. United States Patents 2,796,321, 2,796,322 (18th June 1957).
[19] RÄTZ, R. and HESS, M. *Ber. dtsch. chem. Ges.*, **84**, 889, 1951.
[20] SCHMITZ-DUMONT, O. and KÜLKENS, H. *Z. anorg. Chem.*, **238**, 189, 1938.
[21] CORBRIDGE, D. E. C. *Acta. Cryst.*, **6**, 104, 1953.
[22] BODE, H. and THAMER, R. *Ber. dtsch. chem Ges.*, **76***B*, 121, 1943.
[23] SHAW, R. A. and STRATTON, C. *Chem. and Ind.*, 52, 1959.
[24] KETELAAR, J. A. A. and DE VRIES, T. A. *Rec. Trav. chim. Pays-Bas*, **58**, 1081, 1939.
[25] STEGER, E. *Z. anorg. Chem.*, **294**, 146, 1958.
[26] BASTIANSEN, O., HEDBERG, L., and HEDBERG, K. *J. chem. Phys.*, **27**, 1311, 1957.
[27] CHAPMAN, A. C., PADDOCK, N. L., PAINE, D. H., SEARLE, H. T., and SMITH, D. R. *J. chem. Soc.* (In press.)
[28] BUNN, C. W. and HOWELLS, E. R. *Nature, Lond.*, **174**, 549, 1954.
[29] MAHLER, W. and BURG, A. B. *J. Amer. chem. Soc.*, **80**, 6161, 1958.
[30] MICHAELIS, A. and SCHROETER, G. *Ber. dtsch. chem. Ges.*, **27**, 490, 1894.
[31] CRAIG, D. P., MACCOLL, A., NYHOLM, R. S., ORGEL, L. E., and SUTTON, L. E. *J. chem. Soc.*, 332, 1954.
[32] CRAIG, D. P. *Ibid.*, 997, 1959; in 'Theoretical Organic Chemistry', p. 20, Butterworth, London, 1959; *Chem. Soc. spec. Publ. No.* 12, p. 343, 1958; CRAIG, D. P. and PADDOCK, N. L. *Nature, Lond.*, **181**, 1052, 1958.
[33] CRAIG, D. P. and MAGNUSSON, E. A. *J. chem. Soc.*, 4895, 1956.
[34] NARATH, A. LOHMAN, F. H., and QUIMBY, O. T. *J. Amer. chem. Soc.*, **78**, 4493, 1956.
[35] BEZMAN, I. I. Paper presented at 136th National Meeting, American Chemical Society. September 1959.
[36] HASZELDINE, R. N. and SMITH, F. *J. chem. Soc.*, 603, 1951.

The accretion of cosmic matter to the Earth

H. PETTERSSON

Deep-sea samples taken on the *Challenger* expedition of 1872–76, and analyses of Arctic snow made at about the same time, demonstrated the accretion of cosmic matter to the Earth. Only comparatively recently, however, has it been possible to obtain sufficient samples, corresponding to geologically considerable periods of time, to estimate both the temporal and geographical variation of the fall of matter of cosmic origin. This article reviews the results of recent investigations of long deep-sea cores and of air samples taken at observatories remote from the contaminating effects of the artifacts of industrial activity.

Early in 1874 the Swedish geologist and explorer A. E. Nordenskiöld, famous for his accomplishment of the North-east Passage in the *Vega* in 1878–80, described to the Royal Academy of Sciences in Stockholm [1] a study he had made of samples of snow that had fallen near the city in the previous month. From these he had recovered a small quantity of a dark magnetic powder which proved to contain metallic iron. Subsequently, during Arctic expeditions, he obtained similar material from other samples of virgin snow: analysis showed the presence not only of iron but of phosphorus, cobalt, and probably nickel. Nordenskiöld expressed the opinion that the magnetic material was of cosmic origin. Later, in a more detailed discussion [2], he tried to estimate the total quantity of cosmic dust falling on the Earth's surface. He concluded that the quantity was between half a million and one million tons annually.

Some two years after Nordenskiöld's original description, John Murray—who had lately returned to England on the completion of the famous circumnavigating voyage of the *Challenger*—described the deep-sea deposits that had been recovered during the cruise. He reported that small magnetic spherules could be extracted from deep-sea deposits and from powdered manganese nodules recovered from great depths. As the external surfaces of these particles strongly resembled those of iron meteorites, and as analysis showed them to contain metallic iron, Murray had no hesitation in calling them 'cosmic spherules' [3, 4]. He believed them to be derived from iron meteors, the surface of which had been melted by friction with the air. The drops of iron thrown off from the molten surface quickly solidified, fell into the sea, and eventually came to rest on the sea-bed: because of their slow rate of accumulation, the deep-sea deposits offer a unique opportunity for obtaining these cosmic spherules in substantial quantities. From about a litre of red-clay deposits Murray could obtain twenty to thirty of the spherules, most of them with diameters in the range 0·25–0·03 mm, but some even smaller.

Thus the work of Nordenskiöld and of Murray, some eighty years ago, both demonstrated the accretion of cosmic matter to the Earth and directed attention to two important sources of the particles, the Arctic snows and deep-sea deposits. Neither source, however, is readily accessible, and this delayed further research. In planning the Swedish Deep-Sea Expedition with the *Albatross* [5] in 1946, I attached great importance to the study of magnetic particles in deep-sea deposits [6]. Thanks to the ingenious construction of B. Kullenberg's 'piston core-sampler' [7], we had on board a means of raising from great depths almost undisturbed cores up to, and sometimes exceeding, fifteen metres in length. Figure 3 shows sections from a long core taken from sediment in the eastern Mediterranean: the arrows indicate layers of volcanic ash.

The very slow rate of growth of some deep-ocean deposits makes it possible to estimate the accretion of former ages. In some regions the bottom deposits grow at the rate of only 1–2 mm per thousand years: the long cores now obtainable represent the deposits of some 6–15 million years. If the concentration of cosmic spherules in successive layers of the core is measured, we have a direct means of measuring the accretion from late Tertiary times onward.

To achieve this, however, it was necessary to develop a less crude method of extracting the

spherules than Murray had used: Murray was content merely to stir an aqueous suspension of the sediment with a small permanent magnet. For more effective separation, I eventually decided to acquire a powerful electromagnetic separator, the essential parts of which are a series of circular soft-iron sieves, arranged round an electromagnet energized by a 10-amp current. Weighed samples of the sediment were stirred with an excess of water and passed three times through the magnetized sieve. The current was then switched off, and the particles were detached and collected. The particles were then graded according to size (>250 μ, 250–60 μ, 60–30 μ, and <30 μ) by means of sieves with brass meshes. The particles so isolated were examined under the microscope, and those unequivocally identified as of cosmic origin were counted [8]. The nickel content of the spherules may be taken as a reliable criterion of cosmic origin. A. A. Smales, D. Mapper, and A. J. Wood [12] have recently shown that the Ni : Fe, Ni : Co, and Ni : Cu ratios of spherules from deep-sea deposits are in good agreement with the corresponding values for iron meteorites. Blank experiments, carried out with iron spherules of comparable size—made by heating iron wire in the flame of a blowlamp—mixed with deep-sea sediment from which all magnetic material had been removed, showed that the extraction method had an efficiency of about 95 per cent.

Using this method, worked out in detail by my collaborator K. Fredriksson of the Swedish Geological Survey in Stockholm, we found surprisingly large numbers of typical cosmic spherules in deep-sea sediments, especially in a homogeneous red clay raised from great depths in the equatorial region of the Pacific [9]. Their numbers varied from about one hundred up to several thousands per kilogram of sediment; that is, from ten to a hundred times greater than those Murray obtained from the red-clay samples recovered on the *Challenger* expedition.

Even apart from such criteria as their nickel content, a cosmic origin seems self-evident for the spherules found in deep-sea deposits remote from the continents. The same cannot, however, be said of the magnetic spherules which in recent years have been gathered direct from the atmosphere in surprisingly large numbers, especially by investigators in the United States. It seems probable that here there is contamination with artifacts, particularly the small iron spherules released in vast numbers during welding and other industrial processes: the wind may carry such particles over great distances. If air sampling is used, the samples should be collected in regions as far removed as possible from industrial activity, preferably on remote islands. At the author's instigation, such sampling has recently been started on certain Pacific islands (see later), but it will be a few years before detailed results can be expected. A more critical sampling of atmospheric cosmic dust has lately been undertaken by British investigators [11].

Using an X-ray micro-analyser constructed by R. Castaign in Paris, Fredriksson submitted parts of single spherules (figure 5), obtained during the *Albatross* cruise, to detailed analysis [13]. This showed that whereas the metallic nucleus of one spherule consisted of Fe 68·6, Ni 29·8–31·6, and Co 1·5 per cent, that of another contained Fe 44·4, Ni 53·5, and Co 1·8 per cent.

The following general conclusions emerge from our studies of deep-sea sediments.

1. All the samples investigated show the presence of cosmic spherules in numbers that are very variable but greater than those found by Murray. In general, they range from one hundred to two thousand per kilogram.
2. The variation in numbers depends upon both geographical location and upon depth below the sediment surface; that is, upon the age of the layer. In general, the number of spherules is greatest in the more recent sediments. Nevertheless, substantial numbers of spherules were found in layers of Tertiary age: this contradicts the assertion made by some authorities [14] that no meteors fell on the Earth during that time. Figures 1 and 2 show a comparison of spherule frequency in deposits from the central and west Pacific respectively.
3. The considerable variation in the concentration of spherules in different layers can be explained by the very irregular distribution of meteor-falls over the Earth's surface.

Consideration of the average concentration of spherules in the most recent sediments makes it possible to estimate the present rate of accretion. Our calculations indicate a fall of 1000–5000 tons annually.

Potentially, the analysis of long deep-sea cores allows us to determine the frequency of meteor falls on the Earth over the past several million years. Although the present material is too limited for this to be done, the present intensification of oceanographic research, especially in the United States, gives good grounds for hoping that the

difficulty will soon be overcome. Conversely, if the necessary data are established, the frequency of spherules may be used for dating the different layers of cores. Very intense meteor-falls in the past—such as the famous 'meteor blizzard' of 13th November 1833 (figure 4)—may well have left characteristic marks in the sedimentary record.

Such a method of dating may also be used by scientists working in both the Arctic and Antarctic as a method of dating ice obtained from boreholes, and so of estimating the past rate of growth of the ice. It is probable, however, that to obtain a satisfactory answer the magnetic particles would have to be extracted from very large quantities of ice.

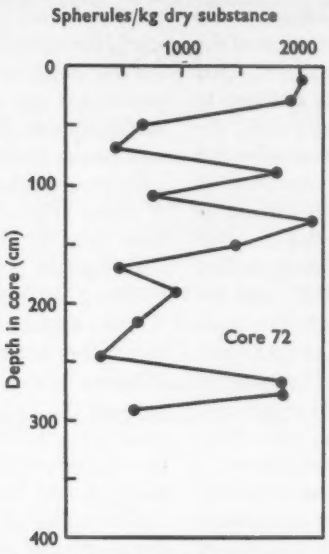

FIGURE 1 – *Distribution of spherules according to depth in a core from the central Pacific.*

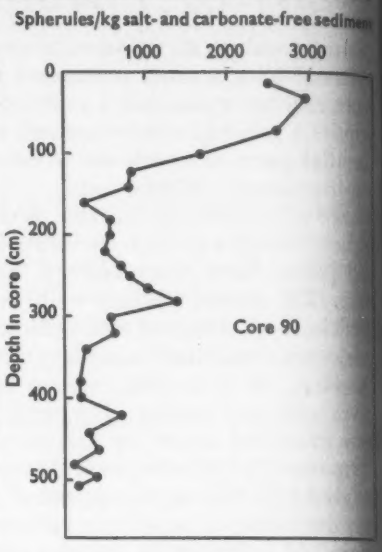

FIGURE 2 – *Distribution of spherules according to depth in a core from the west Pacific.*

If it is possible to realize the 'Mohole' Project [19], which involves a deep boring through the ocean sediments until the underlying rock is encountered, the same method would allow us to estimate the frequency of meteor falls from the time when the oceans were first formed.

THE RATE OF ACCRETION OF COSMIC DUST

By far the greatest part of the meteors incident on the Earth are dissipated in the atmosphere into fine dust, which settles slowly. Apart from rough estimates by Nordenskiöld and others, no measure of the total weight of this dust has been attempted. Two different means are available for obtaining this information, namely, the investigation of deep-ocean deposits and the study of airborne dust.

In 1950 the author, with H. Rotschi [17], advanced the hypothesis that the relatively high nickel-content of Pacific-sediment samples may be due to meteoric dust. Determinations of nickel in deep-ocean cores obtained during the cruise of the *Albatross* have been made by G. R. Berrit and H. Rotschi [15] using chemical methods, and by S. Landergren [16] by spectrographic means. Continental igneous rocks have an average nickel-content of only 0·008 per cent; ocean water contains only 10^{-8} per cent, some five hundred times less than the iron content. Analyses of sedimentary samples show very variable, but relatively high, nickel-contents, in the range 0·044 to nearly 0·1 per cent. The significance of these figures in relation to the total accretion of cosmic dust will be considered later, when we have discussed the more direct approach through measurements of airborne dust.

The rate of accretion of meteoric dust to the Earth could be deduced from the results of passing large volumes of air through fine-pored filters at high altitudes. My tenure of a research professorship in geophysics at the University of Hawaii gave me an opportunity of initiating such research in 1957: the investigation also proved of interest to the United States Atomic Energy Commission, from the point of view of airborne Sr^{89} and Sr^{90}. The observations were made at two high-altitude observatories easily accessible by air from Honolulu: one, at 10 000 ft, is on the island of Maui, the other, at 11 000 ft, on the summit of the extinct volcano Mauna Loa (Hawaii). The apparatus consisted essentially of electrically driven ventilators which forced measured volumes of air through fine filters. The results from the first year's work were, briefly, as follows.

Most of the filters trapped notable amounts of nickel, averaging 14·3 μg per 1000 cubic metres of air. If one assumes the average nickel-content of meteoric dust to be 2·5 per cent [18] it follows that the cosmic-dust content of 1000 cubic metres of air is 0·6 mg. Certain assumptions must be made if we are further to deduce the total weight of cosmic dust falling annually on the Earth: these relate to the rate at which the dust can be expected

FIGURE 3 – *Upper part of a Mediterranean core broken into sections of maximum length* 28 *inches. The top of the core is on the left of the figure. Volcanic-ash layers are marked with arrows.*

FIGURE 4 – *Meteoritic blizzard of* 13*th November* 1833.

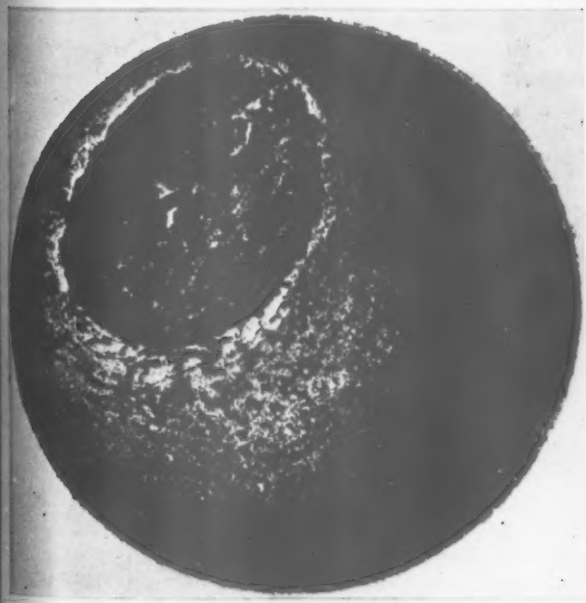

FIGURE 5 – *Spherule with metallic nucleus showing characteristic cupule. (Challenger Rep.: Deep Sea Deposits,* 1891). (×250)

FIGURE 6 – *Cosmic spherules from west Pacific deposits.* (×400)

to fall from the 90 km level, where most of the small meteors are dissipated, to the 3 km level, where the dust was sampled. Plausible assumptions about this lead to the conclusion that the annual rate of accretion of cosmic dust is 5 million tons. This is considerably more than Nordenskiöld's estimate (½–1 million tons) published in 1883, but nevertheless of the same order of magnitude. F. G. Watson [18] estimates the aggregate weight of meteors entering our atmosphere annually as 3·65 million tons. All these computations indicate that the accretion of cosmic dust to the Earth is about a thousand times greater than the accretion of cosmic spherules.

If we accept 5 million tons as a reasonable value for the total annual accretion of cosmic dust, it follows that, on the average, each square centimetre of the Earth's surface receives 0·001 mg annually. In a thousand years the total per square centimetre would be 1 mg, of which 0·025 mg would, on the average, be nickel. These figures are in fair general agreement with our knowledge of the nickel-content of deep-sea deposits. The weight of red clay deposited per square centimetre per thousand years is about 150 mg, and we would expect the percentage of cosmic nickel to be 0·016 per cent. In fact, this is about one-third of the nickel-content of Pacific deposits determined by Rotschi. In certain layers the nickel-content is twice the average: this may correspond to exceptionally heavy meteor falls.

A preliminary investigation of the cosmic spherules present in the upper sections of a core taken from the central Pacific has been carried out at the Oceanographic Institute of Gothenburg [20]: the results have been discussed by E. J. Öpik [21]. The latter puts forward the view that the spherules are derived from the zodiacal cloud, particles of which are fused into nickel-iron droplets by frictional heat in the atmosphere. Öpik supports our view that the excess nickel in deep-sea deposits is of cosmic origin and, in spite of adverse criticism from some sources [22], regards the view as a fruitful working hypothesis.

The accretion of cosmic dust is of interest to meteorologists and climatologists. E. G. Bowen [23] has suggested that heavy rainfall of world-wide occurrence on certain dates is related to dust settling from the higher strata of the atmosphere as the result of heavy meteor showers some thirty days previously: the dust particles would provide nuclei for the condensation of water vapour. If meteoric dust has in fact such an effect on rainfall, it is clear that heavy showers of meteors may have far-reaching climatic effects. Meteoric dust has also been said to influence noctilucent clouds near the 100 km level [24]. There are therefore good practical reasons for further investigation of the atmosphere's content of cosmic dust and the variation of the content with time.

ACKNOWLEDGMENTS

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REFERENCES

[1] Nordenskiöld, A. E. *Övers. Kgl. vet. Akad. Förh.* No. 1, 1874. Stockholm.
[2] *Idem.* 'Studier & Forskningar i Höga Norden', p. 185, Stockholm. 1883.
[3] Murray, J. *Proc. roy. Soc. Edinb.*, **9**, No. 96, 247, 1876–77.
[4] Murray, J. and Renard, A. F. *Challenger Rep.*, **4**, 327, 1891.
[5] Pettersson, H. *Endeavour*, **8**, 182, 1949.
[6] *Idem. Rep. Swed. Deep-Sea Exped.*, **1–4**, 1952–57.
[7] Kullenberg, B. *Ibid.*, **1**, 35, 1955.
[8] Pettersson, H. 'Festskrift T. E. Jansson Broström', Gothenburg, May 1955.
[9] Pettersson, H. and Fredriksson, K. *Pacif. Sci.*, **12**, 71, 1958.
[10] Fredriksson, K. *Univ. Goth. astron. Notes*, 21, 1958.
[11] Parkin, D. W. and Hunter, W. *Nature, Lond.*, **183**, 732, 1959.
[12] Smales, A. A., Mapper, D., and Wood, A. J. *Geochim. Cosmochim. Acta*, **13**, 123, 1958.
[13] Castaign, R. and Fredriksson, K. *Ibid.*, **14**, 114, 1958.
[14] Paneth, F. A. 'Vistas in Astronomy', Vol. II, p. 1686, 1956.
[15] Berrit, G. R. and Rotschi, H. *Rep. Swed. Deep-Sea Exped.*, **6**, 53, 1956.
[16] Landergren, S. *Ibid.*, **7**, 125, 1954.
[17] Pettersson, H. and Rotschi, H. *Nature, Lond.*, **166**, 308, 1950.
[18] Watson, F. G. 'Between the Planets' (second edition), p. 151. Harvard University Press. 1956.
[19] Bascom, W. *Nat. Res. Council. Publ.*, 717, 1959.
[20] Laevastu, T. and Mellis, O. *Trans. Amer. geophys. Un.*, **36**, 385, 1955.
[21] Öpik, E. J. *Irish astr. J.*, **14**, 116, 1956.
[22] Smales, A. A. and Wiseman, J. D. H. *Nature, Lond.*, **175**, 464, 1955.
[23] Bowen, E. G. *Ibid.*, **177**, 1121, 1956.
[24] Millman, P. M. *J. geophys. Res.*, **64**, 2122, 1959.

Breeding new varieties of fruit trees

W. WILLIAMS and A. G. BROWN

The selection of improved crop plants has been an important feature of agriculture from the earliest times. While empirical methods have resulted in many notable successes, the scientific methods of today are much more rapidly productive. This article discusses some major factors involved in modern breeding programmes, with special reference to fruit trees.

Ever since the emergence of settled communities, man has sought to improve cultivated plants by selective breeding. In modern times, the deliberate exploitation of the variability of crop species has come to be regarded as an essential element in the progress of civilization. The greatest attention has naturally been given to plants that make major contributions to man's diet. Crop plants that are harvested for their fleshy fruits rarely come within this category, however, and with few exceptions—notably bananas—their contribution of energy-rich food constituents per unit fresh-weight is low. The temperate tree-fruits—apple, pear, cherry, plum, and peach—can be regarded only as luxury crops whose value lies chiefly in diversifying the eating and drinking habits of communities whose basic dietary needs are already adequately met. It is not surprising, therefore, that qualities of taste and appearance attain a much greater importance in the search for improved fruits than with most other food crops (figure 2). However, although these fruits are certainly eaten mainly for pleasure, by far the largest part of the production is grown for profit. Commercial considerations demand that new varieties must possess not only the qualities that make them attractive supplements to basic foods but those that ensure economic production.

The process of breeding improved forms of cultivated plants is essentially the selection of individuals having desired combinations of genes and their subsequent multiplication for large-scale crop production. Since the tree-fruits are vegetatively propagated, the problems of achieving uniformity and genetic stability that are common to all sexually reproducing populations do not arise: varieties represented by any number of practically identical genotypes can be developed from single, highly heterozygous (hybrid) individuals. Thus the advantages that follow the maintenance of a maximum level of hybridity in naturally outbreeding species can be utilized simply and fully in new selections. Because of their hybrid nature, varieties of tree-fruit species (with the possible exception of certain peaches) do not breed true, and progenies obtained from self- and cross-pollinations present a bewildering array of dissimilar individuals. All attempts to produce homozygous lines of known breeding behaviour, even if they were considered desirable, are precluded by the length of the generation cycle, which varies from five years for cherry trees to as much as fifteen years for apples and pears. Fortunately, however, the breeding behaviour of highly heterozygous parental lines in respect of measurable characters having a low level of genetic dominance is fairly predictable: the mean values for progenies fall reasonably consistently around the mean of the two parents. In practice, when a large number of crosses is considered, deviations which seriously affect predictions based on the relationships between progeny and mid-parental means do not occur. The choice of parents for achieving any given combination of characters can be narrowed down to the very few that justify the efforts involved in hybridization and selection.

OPTIMAL FAMILY SIZE FOR SELECTIVE BREEDING

Owing to the wide range of variation that results from crossing heterozygous parents, even when they are most carefully selected, relatively few individuals express any given character at an acceptable level. When, as generally happens, several characters are selected in combination, the frequency of desirable types among the progeny becomes progressively lower. Although most workers agree that the size of families must be large to achieve successful selection under these circumstances, estimates of optimal family size have in the past been largely the result of guesswork. The numbers considered necessary have increased over the years but appear recently to have become fixed at between 1000–2000 plants per family. Recent estimates based on extensive

experimental results indicate, however, that such numbers are still far too low.

The number of desirable descendants that can be expected as the main product of an apple-breeding programme for polygenically controlled characters is seldom more than 40 per cent of the total [1]; for every additional definable character the figure rapidly decreases. The actual numbers segregating in each class will clearly depend on the particular cross and on the selection standards applied, but a reasonable estimate based on five characters—such as mildew resistance, size of fruit, season of maturity, flavour, and colour of skin—would be 40, 20, 20, 10, and 10 per cent respectively. Assuming independent distribution of these characters in the progeny, families of 6250 plants would on the average yield one individual possessing a combination of the five traits at an acceptable level of expression, and at least one desirable individual would appear by chance in approximately two out of every three such families. On this basis, the objectives of selection would be missed in one out of every three families; this seems to be a tolerable level of failure. If the frequency of success is to be increased from two in every three families to a level of, say, nineteen out of every twenty families, the family size (n) has to be increased to 18 750, according to the formula $\{(N-1)/N\}^n = 1/20$ where $(N-1)/N$ is the rejected fraction of the family.

The importance of family size in tree fruits does not end at this point, however. Definable characters, such as the ones given, are not solely responsible for determining the success of crops that present an aesthetic appeal. In addition there are purely subjective considerations, and these frequently decide the success or otherwise of a selection. Consequently, if there is to be a reasonable chance of final success, a number of individuals adequately expressing the definable characters must be available from which a final choice can be made. On the assumption that five types represent an adequate number from which the selection is made, and that probability of failure is held at one family in three, an adequate family would consist of 31 250 individuals [2]. As with most estimates involving biological processes, this figure must be interpreted flexibly, but all the extensive experimental evidence supporting it indicates that numbers of this order have to be screened in a purposeful breeding programme.

Observation of 30 000 seedlings is a tremendous task in any crop. In woody species such as the tree fruits, it is practically impossible if the seedlings are to be recorded up to the adult stage. Methods have therefore to be developed which will enable large families to be reduced in the early stages of development to a manageable number.

DISEASE RESISTANCE

One field of plant breeding which generally lends itself to efficient screening in the seedling stage is breeding for disease resistance (figure 5). One of the most serious diseases of tree fruit in this country is apple scab, caused by the fungus *Venturia inaequalis*. Resistance to the disease has been shown to exist among several *Malus* species, including *M. prunifolia*, *M. zumi calocarpa*, *M. atrosanguinea*, *M. floribunda*, as well as *M. pumila*, to which cultivated apples belong [3]. In *M. floribunda* the resistance is conditioned by a single dominant gene. A dominant form of resistance, since it is expressed in heterozygotes, allows the character to be transferred from generation to generation without having to re-isolate the homozygous genotype during the programme of transfer, as must be done with characters conditioned by recessive genes. Thus it has been possible, by back-crossing, to transfer resistance from *M. floribunda* on to the gene background of the cultivated apple at a fairly rapid rate. Progeny selections from the third back-cross generation, which combine immunity to *Venturia* with several of the qualities desirable in a dessert apple (figure 3), are already available.

The control of disease by breeding is a struggle between the variability of the host and the variability of the parasite. In several instances of breeding for disease resistance, no sooner had a new resistant form of host plant been discovered and released for production, than a race of the parasite which had hitherto been extremely rare (or even non-existent) assumed epidemic proportions and the newly selected variety of the host was found to be as susceptible as the original type. The most spectacular developments of this kind known so far have been in connection with resistance to *Phytophthora infestans* (blight of potatoes [4]) and *Puccinia graminis* (stem rust of wheat [5]). Several factors enter into the interplay between host and parasite, but the one that most concerns plant breeding and genetics is the ability of certain races of the parasite to overcome the blocks to infection and sporulation presented by otherwise resistant genotypes. The effect of a gene mutation is basically a fairly simple single change in the chemistry of cell metabolism. This has been established in a wide range of organisms and,

in the present context, applies equally to both host and parasite. Resistance mechanisms based on single gene changes in the host can, in these circumstances, be simply neutralized by corresponding changes in the metabolism of the parasite. Clearly, therefore, the resistance of the cultivated apple to *Venturia inaequalis*—provided by the single dominant gene derived from *M. floribunda*—may yet prove to be impermanent, even though the new selections have not hitherto shown any tendency towards susceptibility over a wide range of conditions.

Genotypes possessing several genes responsible for resistance—acting either independently, or in a supplementary and additive system—present a much more complex barrier to the parasite. Fortunately, certain cultivated varieties of apple are known to possess such polygenic mechanisms for scab resistance. In particular, the Antonovka varieties originating from Russia have proved to be highly resistant to scab and to be useful as parents in breeding. Of greater interest, is the demonstration that highly susceptible English apple varieties of good quality, such as Cox's Orange Pippin and Worcester Pearmain, yield a small percentage of resistant genotypes in crosses. The frequency of resistant segregates in the progeny of crosses between such susceptible types is approximately one per cent, and very large numbers of seedlings have therefore to be screened in order to obtain a satisfactory number of resistant seedlings for initial selection. This approach to the problem of scab resistance, in addition to providing a multiple protection against new races of the disease, obviates the repeated backcrossing necessary when small-fruited species with highly astringent flesh (for example, *M. floribunda*) are used as a source of resistance.

SELF-FERTILIZATION

The breeding of disease-resistant forms of fruit, as described here, is simply a question of incorporating existing mutant genes into genotypes that are phenotypically acceptable in respect of other qualities. It occasionally happens, however, that a desired form of variation does not exist, or is not known to exist, among either the wild or cultivated forms of the species. Such was the situation until quite recently in the sweet cherry, *Prunus avium*, in respect of self-fertilization. All existing varieties of the sweet cherry are self-incompatible, and the incompatibility system is governed by a series of alleles at a particular region of the chromosome, which has been symbolized as the 'S' locus. Essentially, the system depends on the inhibition of pollen tubes in styles which carry an S-allele common to both pollen and style. The S-system of incompatibility is common to many species belonging to several different families of plants. In species of *Nicotiana* and in *Trifolium pratense*, the spontaneous mutation to the self-fertility allele S_f, has long been known. Ever since Muller, in 1927, showed that the rate of mutation could be accelerated by treatment with X-rays, it has been realized that mutation of the type $S_1 \ldots _n$ to S_f could be induced by mutagenic agents. D. Lewis [6], in preliminary tests on a species of evening primrose *Oenothera organensis*, showed that the mutation rate to S_f was markedly increased following irradiation of the anthers with X-rays. Owing to the unfailing efficiency of the style in acting as a sieve against non-mutant (incompatible) pollen grains, the mutation could be recovered, even though the rate of mutation following treatment with a dose of 500 r of X-rays was only one in 300 000 pollen grains. The same technique applied to self-incompatible cherry varieties resulted in the recovery of three independent mutations that were self-fertile. The possibility of utilizing self-fertilization as a means of improving the regularity of cropping in the cherry has now been realized (figure 1) and advanced selections are being developed which both are self-fertile and also bear fruit of high quality.

ASSOCIATION OF GENETIC CHARACTERS

Another aspect of the significance of the S-locus in the improvement of the sweet cherry has recently been exposed [7]. As already stated, gene mutations cause a relatively simple single change in the chemistry of cell metabolism. This is probably true, however, only of the initial steps occurring close to the site of the gene on the chromosome. Further along the chain of chemical reactions initiated by the gene, the consequence of the single change becomes more complicated, and the effect of a simple mutation may frequently be observed in many different characters on various parts of the organism. In higher plants, such effects of genes are very difficult to distinguish from independent gene-action at several loci very closely linked on one small segment of the chromosome. For present purposes, however, the distinction between these alternatives is not important. Of immediate interest are the associations of characters that can result following either or both of these genetic mechanisms. A striking association has

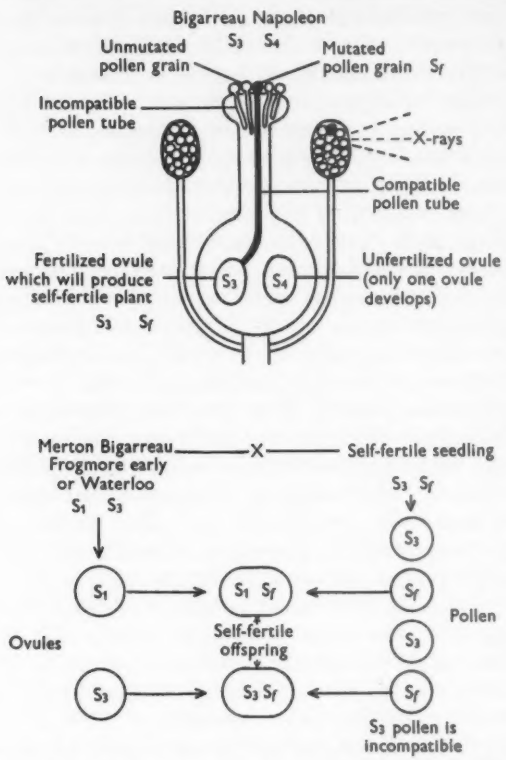


FIGURE 1 – *Two stages in the breeding of self-fertile cherries.*

been revealed in the sweet cherry between certain alleles of the S-locus and the general phenotypic characters that are desirable in improved varieties. An analysis of the most important cherry varieties grown in Europe showed that 65 per cent possess the S_3 allele, 50 per cent S_1, and 39 per cent S_2, while the remaining members of the extensive series of alleles at this locus were shown to be very infrequent. This indicates that during the selective development of the sweet cherry from the wild ancestral species, these three alleles have enjoyed a decided advantage. It has further been shown that certain combinations, in particular S_1S_3 and S_1S_2, have attained frequencies that can best be explained on the basis of selective advantage operating in favour of particular genotypes, quite apart from the S-alleles they contain.

Experimental cherry-breeding confirms these conclusions. Where selection for improved forms has been practised among families which offered an equal chance of either selecting or rejecting individuals containing S_3, the selected individual from each of seven different progenies has possessed S_3 as one of the alleles at this locus. The probability of obtaining such a result by chance is eight times in a thousand families. This strongly supports the view that the S_3 allele itself, or perhaps the chromosome segment in which S_3 is located, has some hidden effect on the characters that have been selected during the evolution of the sweet cherry.

An equally interesting example of an apparently neutral genetic character having a decisive effect on selection is provided by the frequency of alleles at the albino locus in the cherry. This locus is characterized by two alleles, one a recessive which blocks chlorophyll formation and is therefore lethal when homozygous, the other a dominant which governs chlorophyll formation. The recessive allele is present in 51·5 per cent of all varieties investigated, and therefore occupies 26 per cent of the positions available at this locus. Given random mating and absence of selection favouring the heterozygote, a recessive lethal mutation reaches equilibrium with its mutation rate when its frequency equals the square root of the mutation rate. It appears therefore, from knowledge of mutation rates, that the recessive allele at the albino locus in the cherry is well above its equilibrium point. The only satisfactory conclusion that can be derived is that the heterozygote has been preferentially selected during the evolution of cultivated forms of the species.

The genetical significance of these two examples is that they demonstrate the absence of neutrality, during selection, of units of the genetic system, and thus focus attention on the role of the entire genotype as the basic unit of selection. Quite apart from this, the phenomenon can be turned to immediate practical use in cherry breeding. Increased success in the breeding of new forms of the sweet cherry can be expected if the progenies from which selection is made represent S_3 genotypes and are heterozygous for albinism. Several examples showing the same type of response to selection among similar allelic series are known in other fruits, particularly in the peach, *Prunus persica* [8].

EXPLOITATION OF NEW MUTATIONS

Most of the gene mutations that are encountered at low frequencies in natural populations, as well as those that are induced by mutagenic agents, contribute little in the homozygous recessive phase to the fitness of the individual at any given time. The rarity of mutant alleles is simply a measure of their uselessness to the species in its survival over many generations. Mutations that are severely detrimental to survival in the wild are

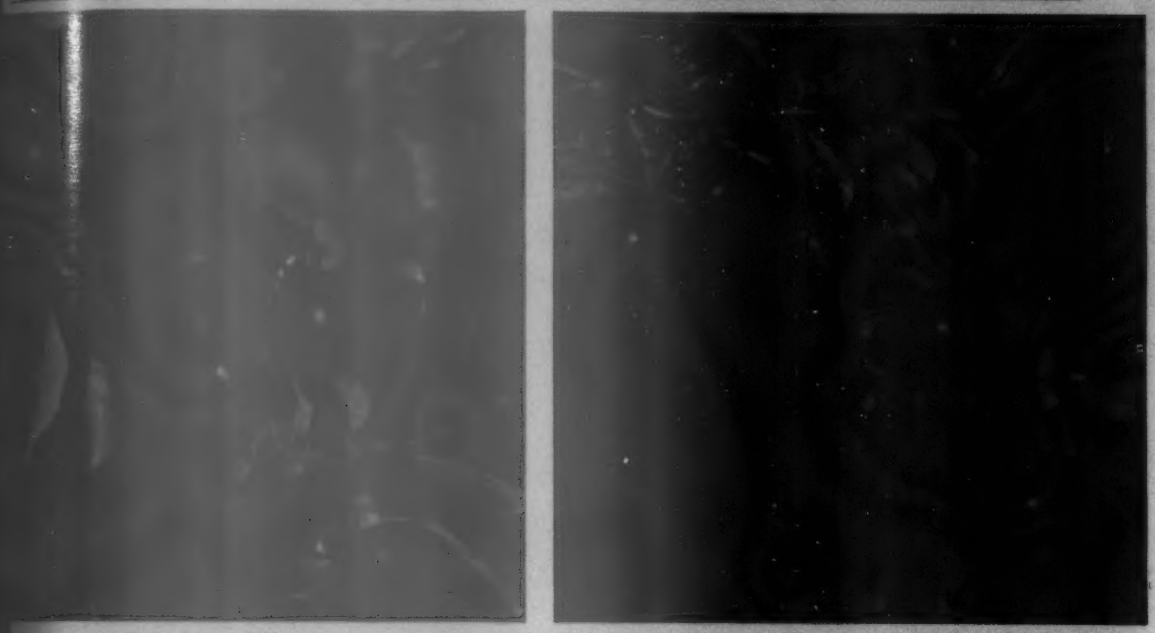


FIGURE 2 – *Left: Merton Worcester, a new variety combining high flesh-quality with a bright red skin. Right: Merton Beauty, a new variety with aromatic flesh.*

generally, and for the same reasons, quite useless in crop improvement. Mutations affecting basic physiological processes such as the chlorophyll-deficient mutations, the various types of lethal and semi-lethal mutations, and those which condition gross morphological changes, belong to this category. There are others which are not severely detrimental to development and survival but which contribute to the success of the species only under special conditions, such as those afforded by cultivation. The mutations which led to the evolution of the non-brittle form of the ear in the bread wheats, thus enabling wheat to be developed as a crop plant, are typical examples of this class of mutation. Others belonging to the same category that may be cited include the mutations to male-sterility in maize, peach, and onion, as well as the mutations to parthenocarpy and seedlessness in the banana [9]. It is therefore evident that even though most mutants are to some degree deleterious in the wild, under the special conditions experienced by cultivated plants, use may be made of both natural and induced mutations for crop improvement.

Clonally propagated perennial species, such as the tree-fruits, lend themselves more easily than the majority of plants to the exploitation of new mutations. Mutant sectors can be detected relatively easily in widely spaced perennial plants, and vegetative propagation permits the rapid multiplication of any useful mutation. Furthermore, since genetical recombination cannot be as fully exploited in woody species with long generation cycles as in annual or biennial species, methods of detecting and inducing somatic mutations have a real place in the improvement of such crops. There are already examples in the apple, where mutant forms of established varieties have achieved considerable economic significance; in some cases (notably the red sports of the apple Delicious) the mutant forms have completely superseded the original variety. Most of the new forms isolated as somatic mutations in tree fruits have either been mutations in skin colour [10] (figure 4)—for example the Red Delicious, Crimson Bramley, and Cherry Cox apples, and the Max Red Bartlett pear—or mutations affecting size of fruit which have in general arisen as a result of the doubling of the chromosome number, as in the tetraploid forms of William and Fertility pears. All the mutations mentioned have appeared spontaneously on the parent varieties and their isolation has been the result of acute observation.

MUTAGENS

A more concerted attempt to exploit somatic

FIGURE 3 – *Stages in the transference of scab r tance from* Malus floribunda *to the culti apple. Top, left:* Malus floribunda. *Top, ri* (Malus floribunda × Rome Beauty) × (Ma floribunda × Rome Beauty). *Bottom, left: F Jonathan. Bottom, right:* (F_2 × *Golden Delici* × *Jonathan.*

(a)

(b)

(c)

(d)

FIGURE 4 – *Bud sports in apple and pear.* (a) *A mutation affecting skin colour which almost covers the entire surface of the fruits.* (b) *Mutations appearing as sectors on the fruit.* (c) *A mutation from non-russet to russet skin following treatment with X-rays.* (d) *A mutation from russet to green skin.*

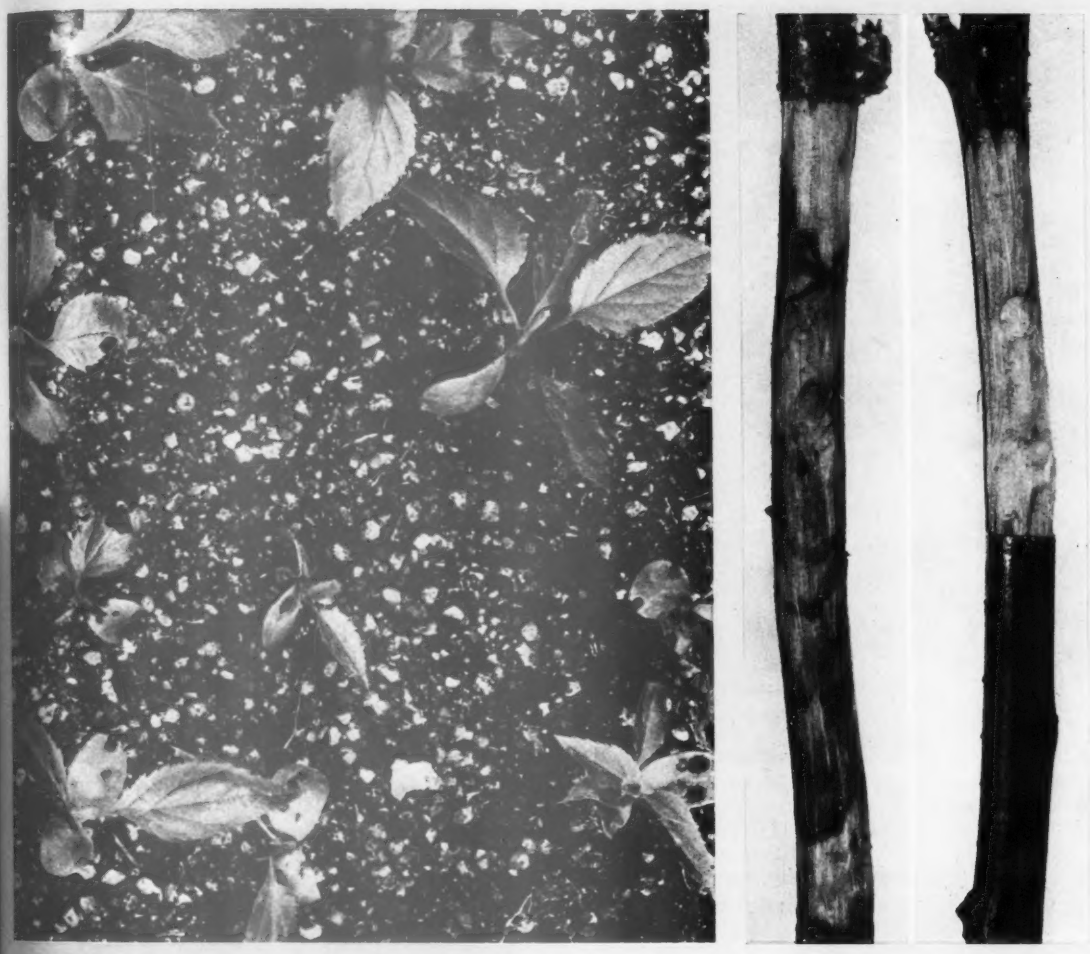


FIGURE 5 – *Above, left: Apple seedlings, showing segregation of scab resistance. Right: Apple shoots infected with collar rot* Phytophthora cactorum. *Susceptible form develops brown lesions under the bark.*

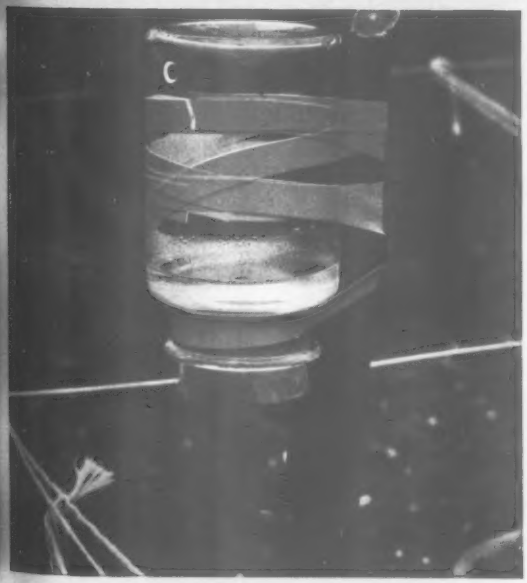


FIGURE 6 – *Injection of a young apple tree with radioactive phosphorus* (P^{32}).

FIGURE 7 – *Seedling cherries, showing segregation of homozygous dwarf genotypes. These have given encouraging re... as dwarfing stocks.*

mutations has been in progress during recent years, and programmes designed to increase their rate of appearance by the use of mutagenic agents are now in progress all over the world. Among the most successful agents for increasing the rate of appearance of mutant somatic sectors are thermal neutrons and X-rays. Gamma rays from a cobalt-60 source and injected radioactive salts are also being used (figure 6). Dormant shoots are irradiated, and techniques of propagation which ensure the development of the youngest primordia on the treated material must be employed [11]. The frequency of recovery of mutant sectors is related to the size of the primordium at the time of irradiation; the smaller the primordium the greater the number of mutants recovered. Success in this field has so far been limited, but the uniformly red sport of the apple variety Cortland, isolated following irradiation with thermal neutrons, promises to be a considerable improvement on the original variety [12]. It is, however, too early to assess generally the ultimate value of methods involving mutagens. For the solution of special problems in certain crops, however, the artificial induction of mutations has almost certainly found a permanent place among the methods of plant breeding.

The appearance of altered sectors following treatment with mutagens is usually accepted as evidence that the mutation has been induced during treatment. In sexually-reproducing short-lived species this interpretation is incontrovertible, but with clonally propagated plants where the somatic tissues live to a great age, the position is not so clear. Over a long period of time, mutations accumulate in the various cell lineages of perennial plants. If a mutation arises in one of the histogen layers of the primordium, the plant may become a chimera composed of layers of differing genetic constitution. Chimeras of this kind are well known, and examples can be cited in apples, pears, and the quince/hawthorn chimera, as well as in potatoes and forms of garden flowers [13]. The mutant forms observed after irradiation of chimerical plants cannot therefore with certainty be ascribed to mutations induced at the time of

irradiation. The high frequency of recovery of identical mutant phenotypes in some vegetatively propagated plants following treatment, indicates very strongly that mutagens such as X-rays affect differentially the rate of survival of the tissues which constitute the various layers in chimeras. If this proves to be generally true, other methods, in particular techniques of propagation which discriminate between the different tissue layers, may prove to be more efficient for the isolation and recovery of the mutant layers.

INFLUENCE OF THE UNDERSTOCK

The improvement of tree fruits where propagation involves the use of an understock is by no means restricted to considerations of the characteristics of the cropping variety itself. Interactions between the stock and the scion can affect profoundly the vigour and general agronomic behaviour of the composite tree. Attention to the breeding and selection of apple understocks for specific purposes by the East Malling Research Station has resulted in immense improvements in the culture and cropping behaviour of apples on a world-wide scale. The development of new types of understocks for the other temperate tree fruits has not been so spectacular. In the cherry, problems of suitable understocks have been particularly difficult to solve. The cherry is a large forest-tree, and rootstocks capable of dwarfing vigorous scions would confer great benefits under cultivation. Related dwarf-growing *Prunus* species generally cause such a crippling stock-scion incompatibility when grafted with *Prunus avium*, that their development for use as dwarfing stocks has now been generally abandoned. Variations within *Prunus avium* which possessed the capacity to induce dwarfing in scion varieties were unknown until quite recently. The recent discovery of a dwarf mutant, conditioned by a single recessive gene present in a large number of cultivated varieties [14], offers new hope of producing dwarfing stocks that are completely compatible with varieties of the sweet cherry (figure 7). Combinations of these dwarfing stocks and new self-fertile selections may, in future, contribute not only to the greater success of the cherry crop in commercial orchards and in private gardens, but also, possibly, to its development as an out-of-season fruit in the private greenhouse.

REFERENCES

[1] BROWN, A. G. *Euphytica*, **8**, 81, 1959.
[2] WILLIAMS, W. *Trans. 2nd Int. Congr. Eucarpia.* (In press.)
[3] SHAY, J. R., DAYTON, D. F., and HOUGH, L. F. *Proc. Amer. Soc. hort. Sci.*, **62**, 348, 1953.
[4] TOXOPEUS, H. J. *Euphytica*, **5**, 221, 1956.
[5] STAKMAN, E. C. *Phytopathology*, **44**, 346, 1954.
[6] LEWIS, D. *Heredity*, **5**, 399, 1951.
[7] WILLIAMS, W. and BROWN, A. G. *Ibid.*, **10**, 237, 1956.
[8] *Idem. Proc. roy. Soc., B*, **145**, 337, 1956.
[9] SIMMONDS, N. W. *J. Genet.*, **51**, 458, 1953.
[10] SHAMEL, A. D. and POMEROY, C. S. *J. Hered.*, **23**, 173, 213, 1932.
[11] BAUER, R. *Hereditas, Lund*, **43**, 323, 1957.
[12] BISHOP, C. J. *Proc. X Int. Congr. Gen.*, **2**, 26, 1958.
[13] CRANE, M. B. and LAWRENCE, W. J. C. 'The Genetics of Garden Plants', (fourth edition). Macmillan & Co. Ltd., London. 1952.
[14] WILLIAMS, W. *Rep. Innes hort. Instn.*, **48**, 7, 1957.

Spider hydraulics

D. A. PARRY

Locomotor systems involving a hydraulic component are common among animals, although such systems suffer from certain limitations. Vertebrates and arthropods have independently evolved a different system, based on skeletal levers, but some arthropods seem to combine the use of a skeleton and hydraulics. This article describes recent work on spiders which has led to this conclusion, and also discusses the implications of such a mechanism for an understanding of the different possible paths of evolution of the arthropods.

The source of power for animal locomotion resides, with few exceptions, in the muscles—aggregates of fibres that can shorten against a load and do mechanical work. Two important requirements need to be met in locomotor systems using muscles. Firstly, the force produced by the muscles must be transferred so as to act between the body and the medium; secondly, provision must be made for re-extending contracted muscles, which cannot actively lengthen. One solution is embodied in many animals which can, from a mechanical point of view, be regarded as muscular envelopes containing a liquid which forms an important component in the locomotor system. The envelope of the earthworm, for example, contains two sets of muscle at right angles, one set encircling the body and the other running along it (figure 1). The tension maintained in these muscles produces a pressure in the contained liquid and so stiffens the animal. The liquid is confined by transverse bulkheads, the septa, so that each region maintains a constant volume. Hence if the longitudinal muscles contract in any region, this region shortens and thickens, and the circular muscles are extended; the reverse is also true, so that a reciprocating system is formed. If the bristles projecting from the body are dug into the soil and withdrawn at appropriate phases of the cycle, the internal muscular forces are transmitted to the environment, and the animal moves forward. Numerous versions of this musculo-hydraulic system account for the movements of such varied animals as sea anemones, roundworms, and snails. The obvious disadvantage of such systems is the coupling that must exist between different muscular activities: when muscles are active in one region of the body, the distribution or pressure of the liquid is altered, and this in turn affects muscles elsewhere. As explained above, the septa afford a partial solution to this problem for the earthworm, but the same situation exists within any one compartment and would seem to preclude the evolution of complex muscular activity.

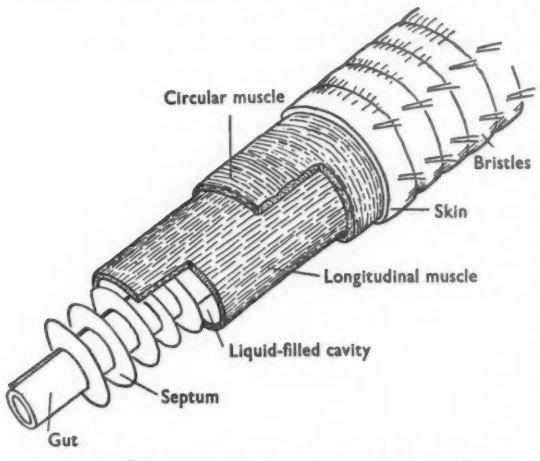


FIGURE 1 – *Schematic diagram of part of an earthworm, showing the body-wall of circular and longitudinal muscles; and the liquid-filled cavity between body-wall and gut, divided transversely by septa.*

Man and other tetrapods show the most elegant of the evolved solutions to the problem of utilizing muscles for locomotion. These animals are supported on jointed struts which act as levers, converting the forces generated in the muscles into propulsive forces bearing on the ground. The configuration and movement of each joint of a limb is controlled by two or more muscles so disposed that when one muscle or group of muscles contracts, the joint moves in one direction, while when the other muscle or group of muscles contracts, the joint moves in the reverse direction and the opposing muscles are re-extended. Some joints, like the elbow joint in man (figure 2), work in one plane only and are controlled by a simple system of mutually opposed muscles. Others, like the shoulder joint in man, are ball-and-socket joints, and their musculature is correspondingly more

FIGURE 2 – (*left*) *The human skeleton* (*after Vesalius* [7]); (*right*) *a diagram of the reciprocating muscle system which operates the elbow joint.*

complicated, as is the control mechanism which activates or deactivates the correct group of muscles for movement in any particular direction.

There is another animal group whose locomotor system is remarkably similar to that of the tetrapods—the arthropods, which includes insects, crustaceans, spiders, and millipedes. As the arthropods constitute a separate line of evolution, it is not surprising to find that their locomotor system, although mechanically similar to that of the tetrapods, is of a different design. Whereas in the tetrapods the stiffness of each limb segment is due to the bone, in the arthropods the stiffness of the segment is due to the cuticle on the outside of the limb, which forms a hollow cylinder enclosing the muscles and other organs. Nevertheless, as in the tetrapods, the limb segments are jointed together; the configuration of the joints is controlled by pairs of muscles, or more complex arrangements, which act reciprocally; and the whole limb acts as a lever whereby the forces generated in the muscles are converted into forces acting between the foot and the ground.

There are, however, exceptions to this similarity. In certain arthropods, notably spiders, scorpions, and other members of the arachnid group, some of the leg joints are so arranged as to exclude the use of muscles in opposition to one another. Figures 3 and 4 illustrate this, by contrasting a normal arthropod joint with a spider 'hinge-joint'. In the former (figure 3), the joint axis passes transversely through the centre of the limb, allowing the attachment of extensor and flexor muscles respectively above and below the axis. In the spider hinge-joint (figure 4), on the other hand, the joint axis runs across the top of the limb, and, as the diagram shows, this allows for flexor muscles but precludes the existence of extensors.

The mechanism which does extend the spider hinge-joint has been investigated recently by R. H. J. Brown and myself [4]. There seemed to be three possibilities. The first, that the hinge-joint is elastic and extends whenever the flexor muscles relax, could be excluded by simple observation: the joint was neutral over a wide angle. The second possibility was that the joint became passively extended through the pressure of the foot against the ground due to muscles acting elsewhere in the leg. This was disproved in the following way. One leg of a living spider was loaded with a small brass ring weighing 45 mg. The spider was held off the ground so that the loaded leg moved in a horizontal plane, unaffected by gravity. When the spider struggled, the hinge-joint of the loaded leg was seen to flex and extend, proving that extension was an active process due to forces generated entirely within the leg itself. Furthermore, by taking a film of the

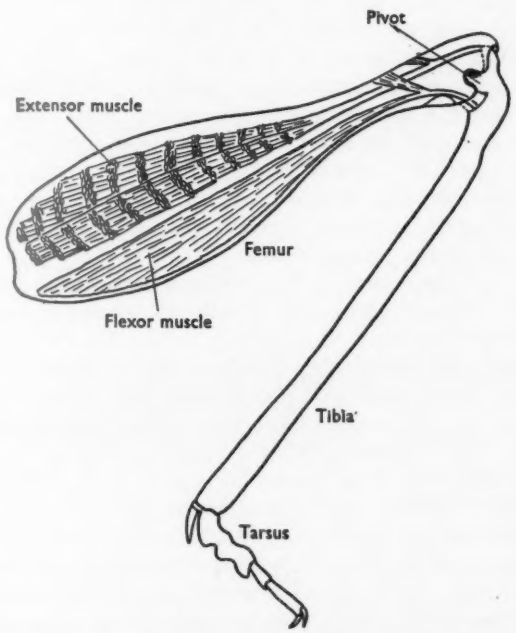


FIGURE 3 – *Diagram of the hind leg of a locust* Locusta migratoria, *showing the extensor and flexor muscles of the tibia and the pivot about which they act.* (*After Albrecht* [1]).

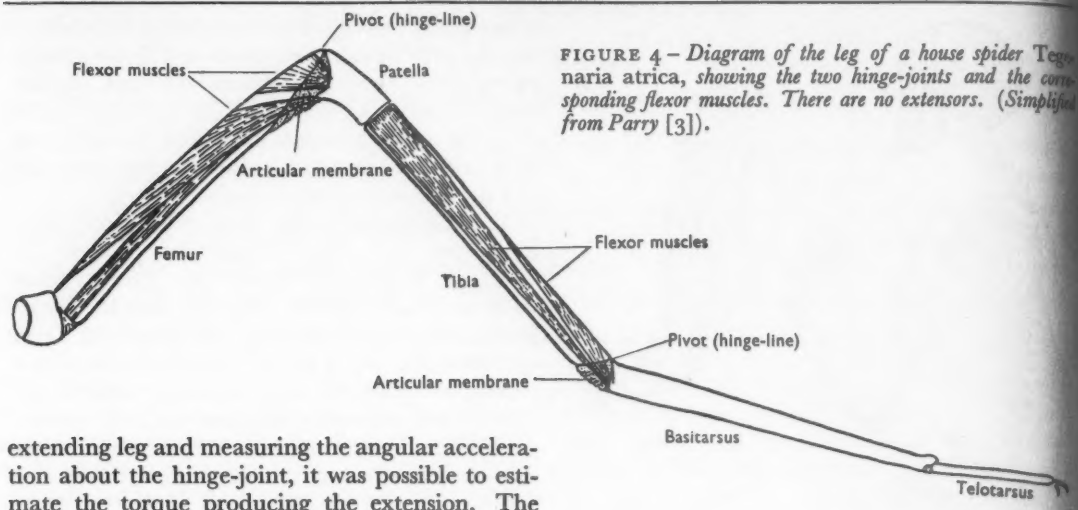


FIGURE 4 – *Diagram of the leg of a house spider* Tegenaria atrica, *showing the two hinge-joints and the corresponding flexor muscles. There are no extensors. (Simplified from Parry* [3]).

extending leg and measuring the angular acceleration about the hinge-joint, it was possible to estimate the torque producing the extension. The use to which such estimates were put will be explained in the following paragraph.

There remains the third possibility. Its nature is suggested by the fact that the volume of a hinge-joint increases with extension: fluid pressure within the leg therefore tends to extend the joint. This can easily be demonstrated by detaching a spider's leg (there is a plane of weakness at the base where the amputation will not cause much loss of blood) and pinching the open end so as to close it and raise the blood pressure: the leg will be seen to extend. The relationship between blood pressure and hinge-joint torque at different angles of extension of the joint was determined using the apparatus illustrated in figure 5. It was found that in order to develop torques of the magnitude shown to arise in the living animal, a blood pressure of some 0·5 atm. was required—a considerably higher pressure than any previously recorded in an arthropod.

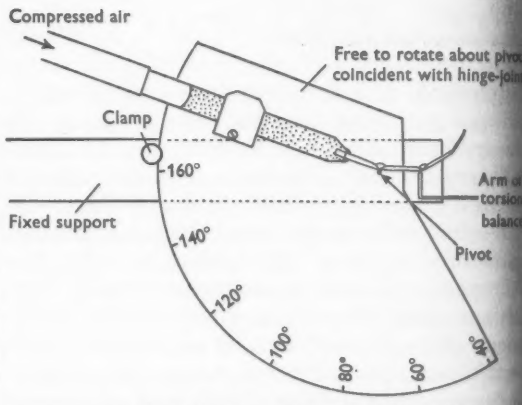


FIGURE 5 –*Method of measuring the relation between the internal pressure of the leg, the joint angle, and the torque developed at a hinge-joint. (After Parry and Brown* [4].)

A simple method, basically similar to that used for humans, exists for directly measuring spider blood-pressure. This depends on the fact that the articular membranes between the leg joints are soft and flexible and therefore collapse as soon as an external pressure applied to the leg exceeds the internal pressure. One leg of a living spider was sealed into a transparent sleeve so that the articular membranes could be observed (figure 6). The pressure in the sleeve was gradually raised and the amount needed to collapse a membrane determined. It was found that the maintained blood pressure of a spider at rest was about 5 cm of mercury—no doubt adequate to extend an unloaded leg, but much too little to account for the results obtained with the loaded leg. However, it

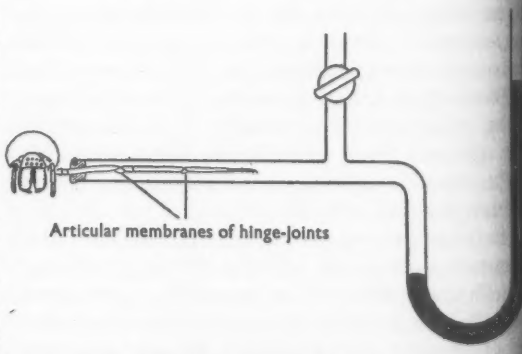
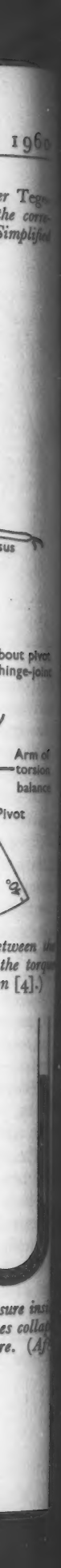
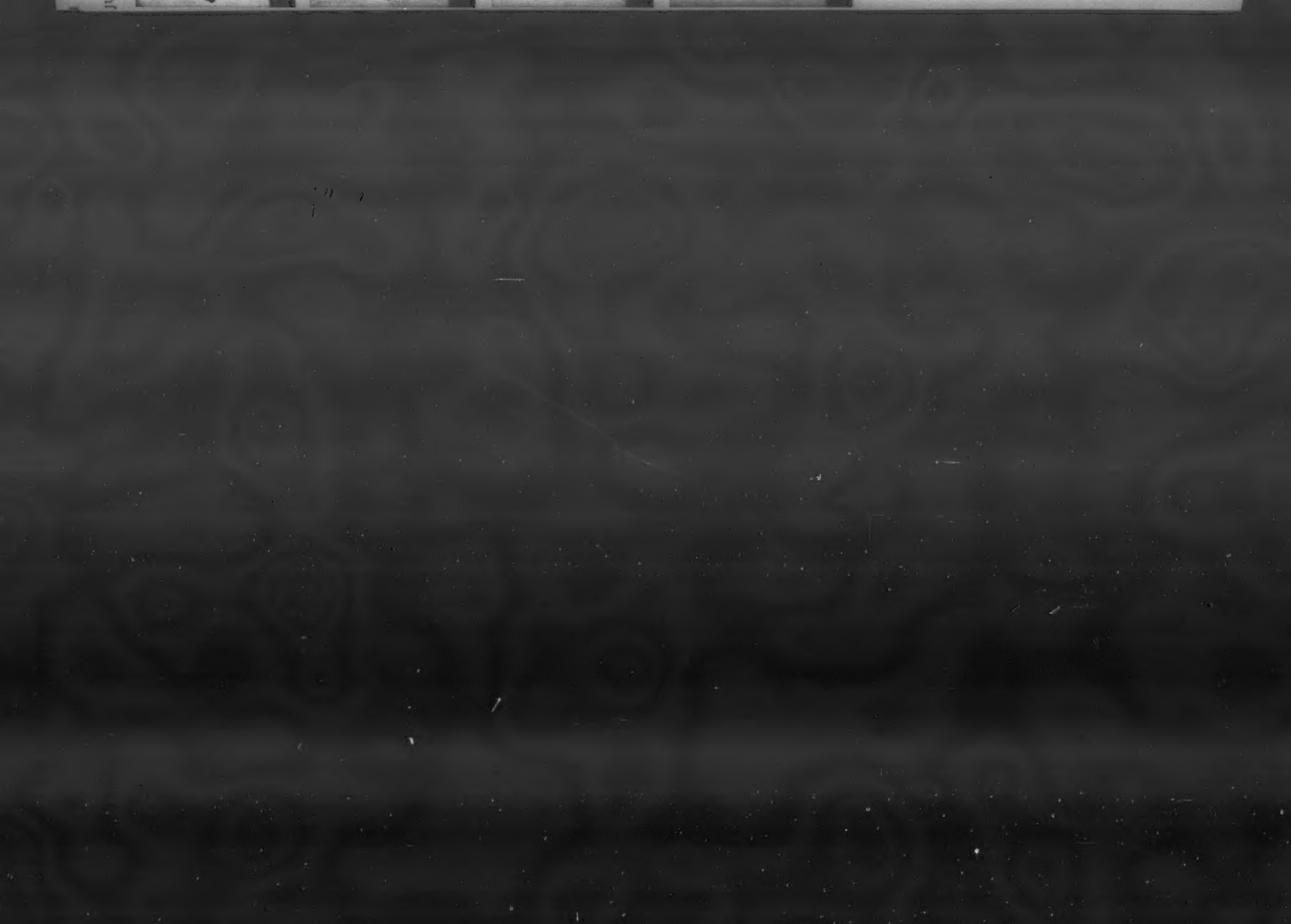


FIGURE 6 – *Method of measuring the blood pressure inside a spider's leg. The hinge-joint articular membranes collapse when the external pressure exceeds the blood pressure. (After Parry and Brown* [4].)





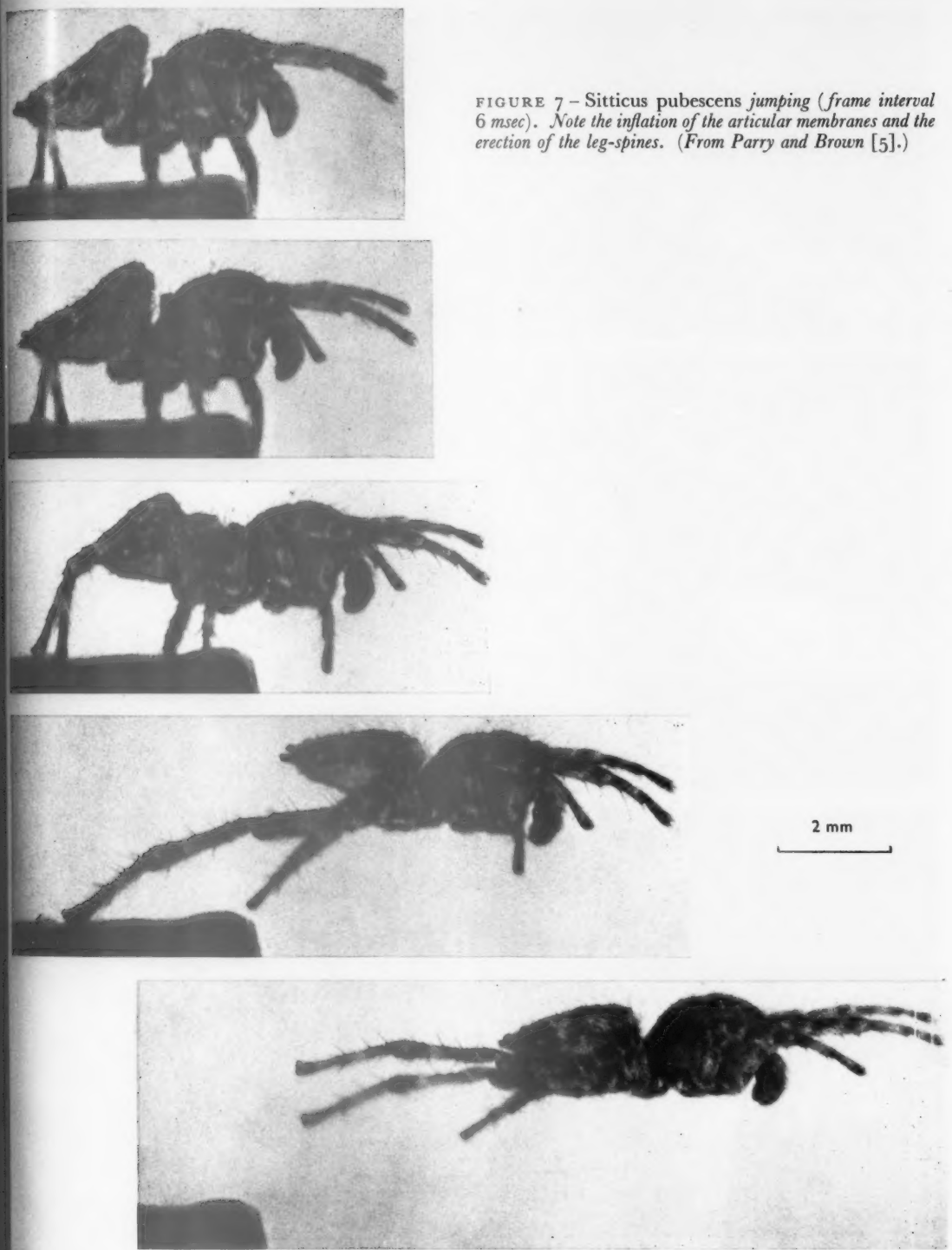


FIGURE 7 – Sitticus pubescens *jumping* (*frame interval 6 msec*). *Note the inflation of the articular membranes and the erection of the leg-spines.* (*From Parry and Brown* [5].)

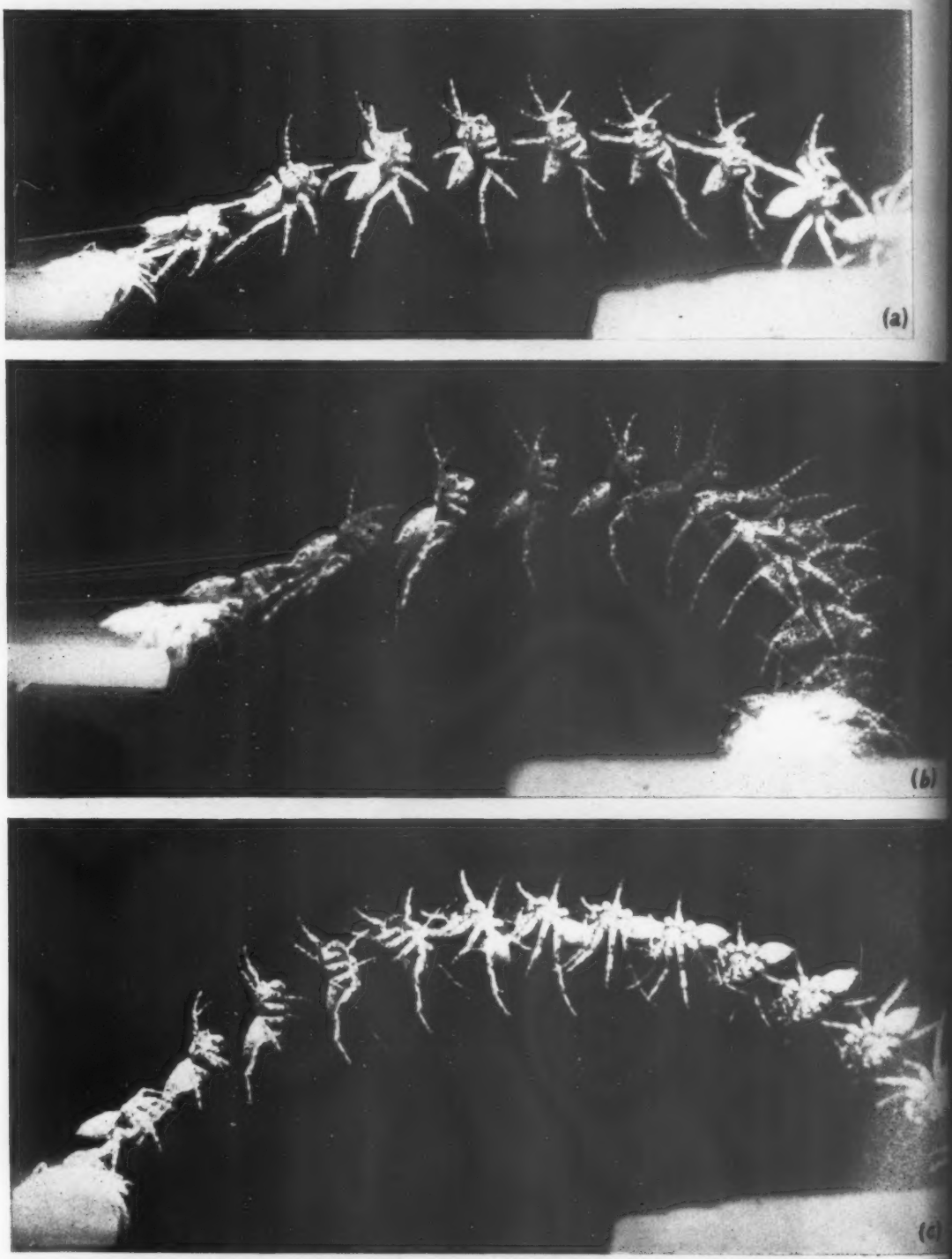
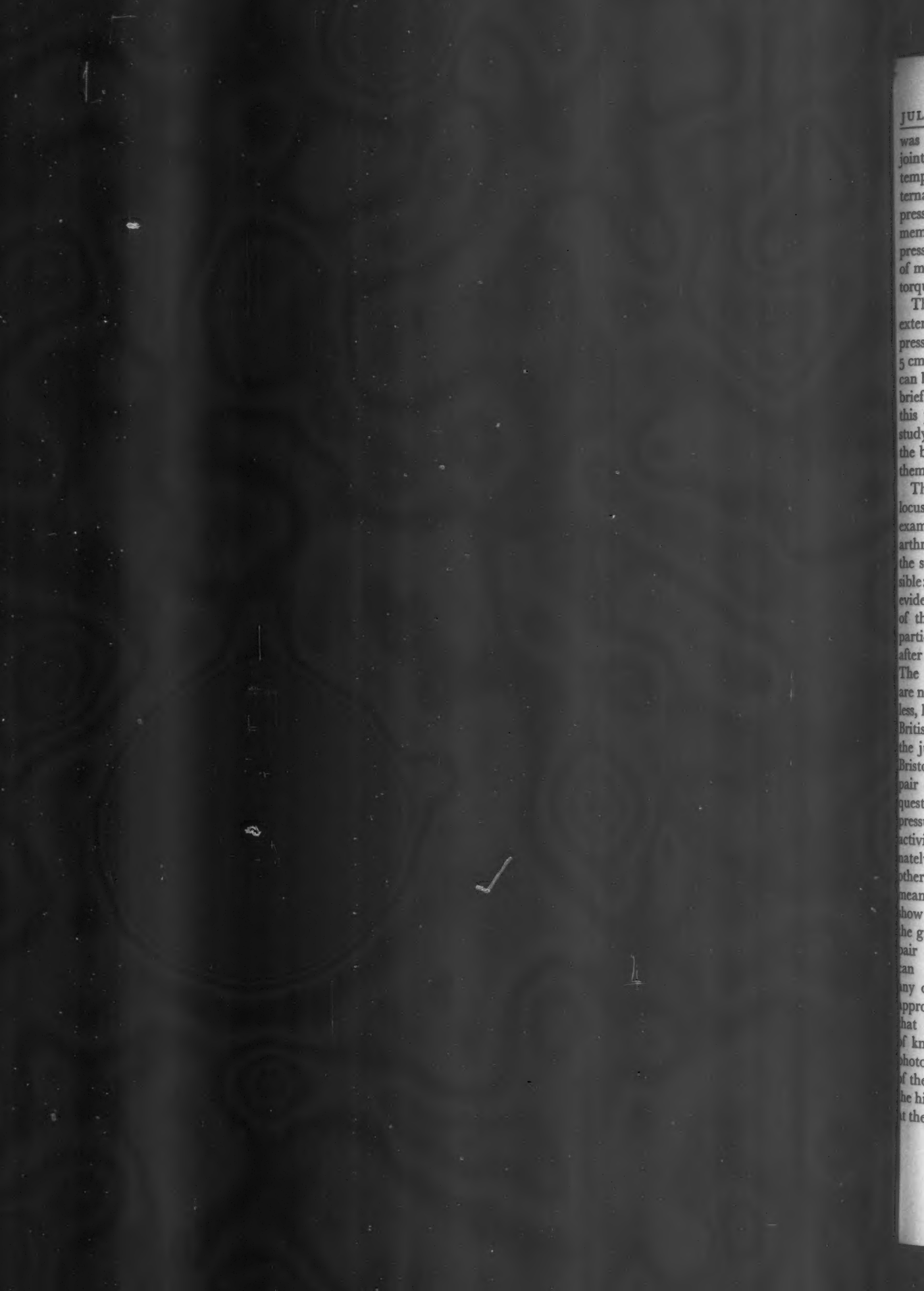


FIGURE 8 – Sitticus pubescens. *Multiple-image photographs (flash frequency 7½ msec) showing the use of the sil dragline in checking 'nose-up' pitch and controlling range. (From Parry and Brown* [5].)



was also found that if a spider struggled after a joint membrane had collapsed, then the membrane temporarily re-inflated, indicating that the internal pressure had risen above the applied pressure. Trials showed that re-inflation of the membrane could take place against an external pressure of up to, but not exceeding, some 40 cm of mercury, which is sufficient to account for the torques measured on living spiders.

These results seem to support the idea that the extension of spider hinge-joints is due to fluid pressure—a pressure which amounts to about 5 cm of mercury in the resting animal but which can be increased to some 40 cm of mercury during brief periods of great activity. How and where this pressure is produced is a matter for further study: there is some evidence that it originates in the body of the spider, and not locally in the legs themselves.

The femur-tibia joint of the hind limb of a locust was illustrated earlier in this article as an example of a normal reciprocating joint of an arthropod (figure 3). When a locust jumps, it is the sudden extension of this joint that is responsible: the great size of the extensor muscles is evident in the figure. Now certain small spiders of the family Salticidae also jump: they have particularly well developed eyes, and leap on or after their prey from distances of 10 cm or more. The legs of these spiders, unlike those of locusts, are not obviously modified for jumping; nevertheless, high-speed flash photographs (figure 7) of the British salticid *Sitticus pubescens* leave no doubt that the jump is in fact due, as was stated by W. S. Bristowe [2], to the sudden extension of the hind pair of legs, especially at the hinge-joints. The question therefore arises as to whether the blood-pressure hypothesis could account for this violent activity. An approach to the problem is fortunately provided by the fact that, unlike some other salticids, *Sitticus* jumps almost entirely by means of the hind pair of legs. The photographs show that the first and second pairs are held off the ground throughout the jump, while the third pair leaves the ground at an early stage, and can in fact be removed altogether without any obvious effect on performance. As a rough approximation, therefore, it may be assumed that the force required to accelerate a spider of known mass at the rate measured from the photographs is equally divided between the feet of the hind legs. Thus, for each configuration of the hind legs shown on the photograph the torques at the hinge-joints can be estimated. These hinge-joints differ from those of the house spider only in size, and the relation between torque and pressure depends only upon size. Hence, using the data obtained on the house spider, the pressure required to produce the jumping-torques of the salticid could be calculated. These calculated pressures fell within a factor of two of those known to occur in house spiders, and in view of the very approximate nature of the calculation the results were considered to support the idea that the salticid's jump was due to hydraulic forces.

The photographs unexpectedly provided direct evidence that the jump was accompanied by a rise in pressure. It can be shown, by pinching the detached legs of many species of spider, that an increase in fluid pressure in the leg causes the leg-spines to erect. Figure 7 shows that this is precisely what the leg-spines of the jumping spider do at the moment of take-off. Furthermore, it appears that the spines on all the legs become erect; note especially those in the first pair of legs, which take no part in the jump. This strongly suggests that the increase in pressure which occurs at the moment of take-off arises in the body itself, or at least in the front half of the body, and affects all the legs equally.

Multiple-image photographs (figure 8) throw further light on the jump. Figure 8a shows that a silk thread, attached near the point of take-off, is drawn out of the spinnerets during the jump; it can be seen bridging the gap across which the spider has jumped. The spider takes off with a pronounced 'nose-up' pitch which is checked before landing: the checking is presumably due to tension in the thread. In figure 8b the same reversal in the initial nose-up pitch can be seen, but towards the end of the jump the thread is put to a more dramatic use, and the spider drops almost vertically downwards. Finally, figure 8c shows what happens when the initial pitch is not checked, presumably because the thread is unsecured (an indication that it has become free can be seen in the photograph): the animal turns an almost complete somersault.

Biologists are inclined to ask two questions

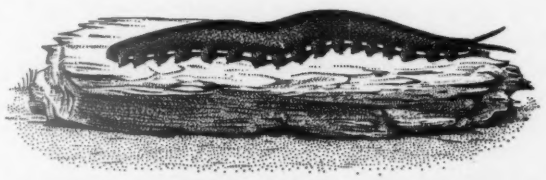


FIGURE 9 – Peripatopsis capensis. (*After A. Sedgwick* [6].)

about an animal mechanism: how does it function, and how has it evolved? Reasons have been given for believing that spider hinge-joints function through flexor muscles acting in opposition to fluid pressure; it remains to consider how such a mechanism can have arisen in evolution. In such a consideration the general principle must be borne in mind that animal mechanisms need to be fully functional and competitive throughout the period of their evolution. It is widely held that arthropods were derived, well over 500 million years ago, from elongated soft-bodied animals with simple lobe-like appendages. Such an animal is most likely to have moved by the musculo-hydraulic principle mentioned at the beginning of this article. This view is strengthened by the existence today of some animals (the group *Onychophora*) of very much this type (figure 9); they could even be modified relics of the original 'pro-arthropods'. They possess a cuticle chemically similar to that of a modern arthropod, but thin and unhardened so that it does not constitute a skeleton. As in arthropods, the spaces within the body are filled with blood, and it is likely that the pressure of the blood stiffens the body and the lobe-like legs. The latter swing to and fro during walking by the action of muscles at their base, and shorten by means of internal muscles acting against the fluid pressure.

If the soft-bodied arthropod ancestor (the 'pro-arthropod') operated on lines such as these, its evolution into an arthropod would involve the gradual hardening of the cuticle (perhaps originally as a protective adaptation) and its conversion into a rigid skeleton. In the limbs at least, this hardening must have been accompanied by the development of joints with bearing surfaces (articulations), and it is not difficult to suppose that the leg musculature became modified into a reciprocating system. Once such a system has been achieved, blood pressure would cease to play any part in the animal's mechanics and the condition would be reached which is seen today in the majority of arthropods.

There seem to be two possible modes of evolution of the hinge-joint. One, in which the hinge-joint was a secondary development from the two-muscle joint, raises difficulties. The selective advantage of such a development is not clear, and the intermediate stages during which the joint axis was shifting and a blood-pressure mechanism re-developed are not easy to visualize. The alternative possibility, that the hinge-joint was independently derived from the pro-arthropod condition, avoids these objections: a lobe-like appendage stiffened by blood pressure can readily be thought of as hardening its cuticle and evolving hinge-joints which were flexed by muscles but continued to make use of blood pressure for re-extension. This suggestion has interesting implications concerning the evolution of the arthropod group as a whole—a subject of extended controversy. Broadly, there are two hypotheses. One is that the soft-bodied pro-arthropod ancestor gave rise to a single type of primitive arthropod—a hardened, jointed animal—from which all arthropod groups were eventually derived. The other is that two or more arthropod groups were independently evolved from the pro-arthropod ancestor. The presence of hinge-joints among arachnids gives some support to the idea that this group at least may be the product of such an independent line of evolution.

REFERENCES

[1] ALBRECHT, F. O. 'The Anatomy of the Migratory Locust'. The Athlone Press, London. 1953.

[2] BRISTOWE, W. S. 'The Comity of Spiders', Vol. II, 231. Ray Society, London. 1941.

[3] PARRY, D. A. *Quart. J. micr. Sci.*, **98**, 331, 1957.

[4] PARRY, D. A. and BROWN, R. H. J. *J. exp. Biol.*, **36**, 423, 1959.

[5] *Idem. Ibid.*, **36**, 654, 1959.

[6] SEDGWICK, A. *Quart. J. micr. Sci.*, **28**, 431, 1888.

[7] VESALIUS. 'Tabulae anatomicae sex'. 1538. From a facsimile edition privately printed for Sir W. Stirling-Maxwell. London. 1874.

Nuclear structure

J. HAMILTON

Although many major questions remain to be answered, recent research makes it possible to discern some systematic pattern in the structure of the atomic nucleus. Despite there being some puzzling features, it seems that the protons and neutrons of which the nucleus is composed move freely in orbits about the centre of mass, in a manner analogous to the orbital movement of electrons around the nucleus. This article reviews the experimental evidence for the structure of the nucleus and discusses its relevance to the shell model.

COMPARISON OF ATOM AND NUCLEUS

The nucleus is the small body, having a radius of about 10^{-12} cm, that lies at the centre of an atom. It is made up of Z protons and N neutrons. $A = N + Z$ is called the atomic weight, and is approximately the weight of the nucleus in units of the proton's mass. Since the neutron is uncharged, the charge of the nucleus is Ze, arising from the Z protons. Apart from the fact that the proton is charged, protons and neutrons have very similar properties, and it is convenient to use the term nucleon to denote either a proton or a neutron.

The mass of a nucleus is not exactly A times the mass of the proton, firstly because the neutron is 0·14 per cent heavier than the proton, and secondly because Einstein's equation, $E = Mc_2$ (where E is energy, M is mass, and c is the velocity of light), means that a tightly bound nucleus is a little lighter than a loosely bound nucleus containing the same particles. If M_{nucl}, M_{p}, and M_{n} are the observed masses of the nucleus, a proton, and a neutron respectively, the binding energy B is given by

$$B = c^2(ZM_{\text{p}} + NM_{\text{n}} - M_{\text{nucl}}) \quad \ldots . (1)$$

The problems of nuclear structure are easier to appreciate if we compare the nucleus and the atom. The radius of the nucleus is smaller than the radius of the atom by a factor of about 10^{-5}. This is much the same as the ratio of 100 metres to the radius of the earth. The binding energy of a nucleus is greater than the binding energy of the corresponding atom by a factor of roughly 10^5 or 10^6. For example, the differences between the energy levels in light nuclei are of the order of 1 MeV, whereas the energy levels in light atoms differ by energies of the order of 10 eV or less. It is this great disparity between the energy tied up in a nucleus and the energy tied up in an atom that makes nuclear explosives so much more powerful than conventional ones.

The atom contains Z electrons, each having a mass about 1/2000 of that of the proton, moving in orbits around the nucleus. The A nucleons in the nucleus are always in motion, but since they all have the same mass and are constantly in collision with each other, we would not expect them to have simple orbits. The atom is held together by the electrostatic (Coulomb) force, which attracts the negatively charged electrons to the positively charged nucleus. When an electron is at distance r from the nucleus this force is Ze^2/r^2. In the nucleus there is an electrostatic repulsion between the protons. The nucleus must therefore be held together by some new force which is unknown to classical physics or chemistry: gravitation is too weak to bind nuclei, for it is too small by a factor of 10^{37}.

This new force—we shall call it the nuclear force—must be attractive, and it must be an order of magnitude greater than the Coulomb force between two protons. We know this because there exist stable nuclei which contain many protons: Pb^{208}, for example, contains 82 protons. We believe that the nuclear force acts between all pairs of nucleons in the nucleus.

THE DISTRIBUTION OF ELECTRONS AND NUCLEONS

The distribution of electrons in the atom is very different from the distribution of nucleons in the nucleus. In the atom only the innermost electrons experience the full attraction Ze^2/r^2 to the nucleus. They move in Bohr orbits of radius $a_{\text{s}} = \hbar^2/me^2Z = 5{\cdot}3 \times 10^{-9}/Z$ cm, where $2\pi\hbar$ is Planck's constant and m is the mass of the electron. The binding energy of these innermost electrons is $me^4Z^2/2\hbar^2 = 13{\cdot}6Z^2$ eV. Electrons which are farther away from the nucleus do not experience the full Coulomb attraction because they are shielded from the nucleus by the inner electrons. Indeed, the outermost electrons experience an attraction

to the nucleus which is little greater than e^2/r^2. Hence these outer electrons have orbits whose radii and energies are, to a first approximation, independent of the atomic number Z.

There are several important consequences of this:

(*A*i) The density of electrons in the atom is not uniform: there are many more electrons per unit volume near the nucleus than in the outer parts of the atom.

(*A*ii) The volume occupied by the free atom does not show any systematic increase with increase in Z; the variations in volume from one element to another are more related to the column the element occupies in the Periodic Table.

(*A*iii) The total binding energy of the electrons is determined mostly by the innermost electrons, and it increases with Z roughly as $Z^{7/3}$.

Now let us look at the corresponding properties of the nucleus. From a variety of experiments we know the following:

(*N*i) The density of nucleons in a large nucleus is uniform from the centre out to a fairly thin surface-region, where it falls off to zero rapidly but smoothly.

(*N*ii) The radius of most nuclei is given by the formula

$$R = r_0 A^{1/3} \qquad \ldots . (2)$$

where r_0 is a constant ($\simeq 1{\cdot}2 \times 10^{-13}$ cm). Thus the volume of the nucleus is $(4\pi/3)Ar_0^3$. This shows that the density is independent of the atomic weight A.

(*N*iii) The total binding energy B of stable nuclei is almost proportional to A. This can be seen by plotting B/A, the binding energy per nucleon, against Z (figure 1). From $A = 20$ to $A = 160$ it is just over 8 MeV per nucleon. For $A > 160$ it falls off slightly, because the Coulomb repulsion between the 70 or 80 protons in these large nuclei becomes more important. For $A < 20$ it falls off because light nuclei are almost all surface and have no uniform interior-region.

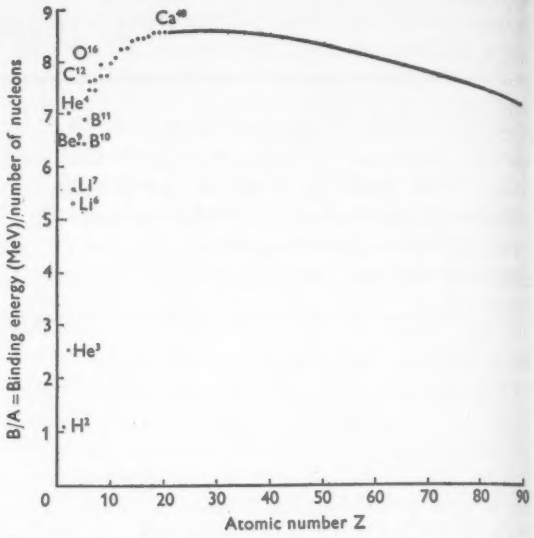


FIGURE 1 – *The binding energy per nucleon of stable nuclei plotted against the atomic number.*

SATURATION OF NUCLEAR MATTER

In each respect, the nuclear properties (*N*i), (*N*ii), (*N*iii) are noticeably different from the corresponding atomic properties (*A*i), (*A*ii), (*A*iii). It appears that the properties of nuclear matter are to a large extent independent of the number of nucleons in the nucleus. If we double the amount of nuclear matter, we merely double the volume of the nucleus and double its total binding energy. These properties are more akin to the properties of a liquid than to those of the electronic structure of atoms.

The cohesion of liquids is due to the attractive force occurring between neighbouring molecules whose separations are no more than a few times their radii. When two molecules come closer together so that their electron shells touch, there is a strong mutual repulsion. This combination of the strong short-range repulsion, and the longer-range attraction between neighbouring molecules makes it possible for any drop of the liquid (containing a sufficiently large number of molecules) to have a unique density which is independent of the total number of molecules in the drop. We use the term saturation to express the fact that adding more molecules does not increase the density or the cohesive energy per molecule.

Clearly the nucleus shows a similar saturation phenomenon. The existence of this saturation in the nucleus implies that the nuclear force cannot be an attractive force acting between each pair of nucleons at all separations. A simple calculation shows that if this were so, a 'collapsed state' of the nucleus would be energetically favoured. In this collapsed state each of the A

nucleons lies within the range of the attraction of all the others. This gives a total potential energy which is negative and varies as A^2. The total kinetic energy is positive, and for the collapsed state can be shown to be proportional to A, if we ignore the exclusion principle. This principle states that two or more nucleons cannot occupy the same wave-mechanical state. This principle certainly cannot be ignored in the nucleus. When it is applied to the collapsed state, it requires some nucleons to be in states of greater momentum than would otherwise be the case. As a result, the kinetic energy in the collapsed state is proportional to $A^{5/3}$ instead of to A. For $A > 20$ the potential energy is predominant, therefore the total binding energy of a medium or large nucleus should vary as A^2, whereas in (*N*iii) we saw that it varies as A. Also, the calculated value of the binding energy in the collapsed state is much greater than the observed values. It follows that actual nuclei are not in the collapsed state, and hence the force between each pair of nucleons must become repulsive at some separation: it cannot be attractive at all distances.

SATURATION AND THE NUCLEAR FORCE

The concept of the saturation of nuclear matter is so fundamental to our understanding of nuclei that we would like to be able to give a simple explanation of its occurrence. Unfortunately, saturation is not the direct result of any single fundamental principle of physics, and we have to examine several phenomena in detail before we begin to see how it comes about.

First, we examine the nature of the force between two nucleons—that is, the nuclear force. Here we can use direct experiments. High-energy protons or neutrons, produced by a cyclotron or synchrotron, can be scattered by protons which are initially at rest. Scattering-experiments carried out with protons and neutrons of various energies will yield considerable information about the nucleon-nucleon forces. We then make the important assumption that the force between two nucleons inside the nucleus is the same as the force between the two nucleons when no other nucleons are present.

For practical reasons we cannot in this way find the force between two neutrons. Instead we deduce this force by the principle of charge symmetry, which states that the force between two neutrons is identical with the force between two protons if the Coulomb repulsion is ignored. The evidence for charge symmetry comes from mirror nuclei: replacing all the protons and neutrons in a nucleus by neutrons and protons respectively gives the mirror nucleus. Examples of mirror pairs (mostly involving nuclei which are unstable against β-decay) are H^3, He^3; He^5, Li^5; Be^{10}, C^{10}; B^{11}, C^{11}; C^{13}, N^{13}; C^{14}, O^{14}; and O^{18}, Ne^{18}. It is easy to calculate the difference in the Coulomb energies of the two members of a mirror pair. When this has been allowed for, it is found that the energies of the ground state and of the excited states of the two members of any mirror pair are almost identical. Other properties of these states, such as their spins and parities, are also identical (figure 2). In other words, exchanging the protons and neutrons in a nucleus alters only the Coulomb energy (and the other electromagnetic property, the magnetic moment); this proves charge symmetry.

THE HARD CORE

In the light of the principle of charge symmetry, the scattering experiments show that the forces between any two nucleons are attractive at separations of the order of 10^{-13} cm, but that at separations shorter than $0{\cdot}4 \times 10^{-13}$ cm the forces become very strongly repulsive. This region of strong repulsion at short distances is known as the hard core.

At first sight it would seem that the hard core,

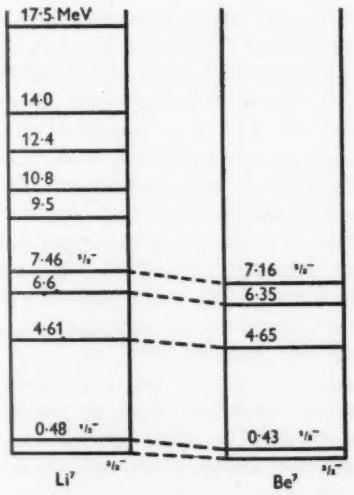


FIGURE 2 – *The known energy levels of the mirror nuclei Li^7 and Be^7. The energies of the excited states above the ground states are given in MeV. The plotted levels have been adjusted by subtracting the Coulomb energy difference. The spins and parities are given where they are known. Dotted lines join corresponding states.*

together with the attraction at longer ranges, is just what we require to explain the saturation of nuclear matter. Unfortunately, when we examine the situation in detail we find that this nucleon-nucleon force would give saturation only at a density which is about ten times the observed density of nuclear matter. In other words, the hard core does not have a sufficiently great radius to account by itself for the observed nuclear saturation. For a complete explanation of saturation we shall have to look for other properties of the nuclear force.

EXCHANGE FORCES

Another important property of nuclear forces is their exchange nature. The idea of exchange forces was originally put forward by Heisenberg and Majorana as an analogy with the chemical force between two hydrogen atoms. In the chemical case the exchange force appears when two requirements are satisfied (*a*) the electrons must obey the exclusion principle, (*b*) the wave function for the two electrons must have certain simple symmetry properties. This results in there being an appreciable probability that the two elctrons lie in the region between the two protons, and it gives rise to the valence bond. It is reasonable to regard this force as arising from the exchange of the electrons between the two atoms. There is no analogue to this exchange force in classical physics.

The exchange force between two hydrogen atoms is attractive if the wave function of the two electrons is unaltered when the positions of the two electrons are interchanged (a symmetric wave-function), and it is repulsive if the wave function changes sign under this interchange (an anti-symmetric wave-function.) The potential energy of the interaction is therefore of the form $V(r)P_x$, where P_x is an operator which exchanges the positions of the two electrons. Acting on a symmetric wave function, P_x multiplies it by $+1$, while it multiplies an antisymmetric wave function by -1.

It is suggested that the potential energy of the interaction between two nucleons (at separations $r > 0{\cdot}4 \times 10^{-13}$ cm) is of the form $V_0(r) + V_e(r)P_x$. Thus if the two nucleons are in a state which is spatially symmetric, the potential energy is $V_0(r) + V_e(r)$; if the state is spatially antisymmetric the potential energy is $V_0(r) - V_e(r)$. It is therefore quite easy to arrange that, at separations of the order of 10^{-13} cm, two nucleons have a strong mutual attraction if they are in a spatially symmetric state, whereas they have no attraction, or are repelled, if they are in a state which is spatially antisymmetric. There is a good deal of evidence that the nuclear force has this particular behaviour; we shall now examine its consequences.

THE EXCLUSION PRINCIPLE AND SATURATION

As we have seen, the exclusion principle states that two nucleons cannot be in exactly the same state. Each nucleon has four internal degrees of freedom; this is because each nucleon has two possible charge values (corresponding to being a neutron or a proton) and two possible spin values (corresponding to the spin being up or down relative to an arbitrary direction). Therefore the exclusion principle states that at most four nucleons can have an identical spatial wave function—these four nucleons are two protons with opposite spins and two neutrons with opposite spins.

The exclusion principle together with the exchange nature of the nuclear force could give nuclear saturation. The following is a simple—if crude—way of seeing how this comes about. Suppose a number of nucleons are placed very close together. The exclusion principle allows us to have up to four nucleons at one point, but it will not allow a fifth nucleon to be there. In other words, the wave function of the fifth nucleon must vanish at the position of the other four. The simplest way in which this can happen is that the wave function should be antisymmetric against exchange of the fifth nucleon with any of the first four. Therefore, though the nuclear force can exert a strong attraction between the first four, on account of the exchange property, the fifth will not be attracted by any of them. This behaviour is sufficient to give saturation, since it gives rise to a potential energy which will vary only as A.

A more careful treatment shows that this crude explanation is indeed valid. Further, we expect that a combination of the hard core at short ranges, and exchange forces at longer ranges, should make it possible to explain the observed nuclear saturation. However, this leads to a difficult mathematical problem which has been only partially solved. It is necessary to treat the wave-mechanical motion of each nucleon under the influence of its known interactions with all the others. Also, this difficult many-body problem has to be solved taking account of the exclusion principle. The result should give the

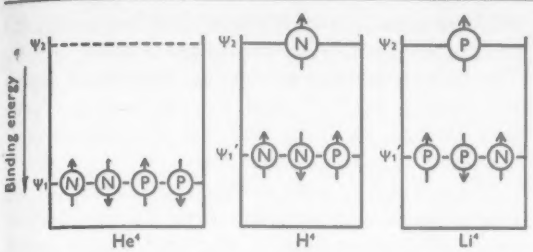


FIGURE 3 – *The independent-particle model for He^4, H^4, Li^4. The exclusion principle plays an important role in determining the stability of these nuclei.*

observed density of nuclear matter and the observed binding energy per particle. Although K. A. Brueckner has made important advances in this direction, we still seem to be far from anything like an adequate solution of this fundamental mathematical problem.

NUCLEAR SYMMETRIES

The exclusion principle and the exchange nature of the forces also help to explain some of the simple symmetries that are observed in stable nuclei. We have space to give only the simplest example—why He^4 is tightly bound, while no other nuclei with $A=4$ exist. We can begin to understand this situation if we remember that the exclusion principle will allow all four nucleons in He^4 to be in the same spatial state ψ_1 (see figure 3). Each nucleon is then strongly attracted to the other three and a tightly bound nucleus results. If we try to form other nuclei having $A=4$, such as H^4 or Li^4, the exclusion principle allows only three of the nucleons to be in the lowest state ψ'_1 (compare figure 3). This state has less binding energy than has ψ_1, because there are only three attracting pairs, compared with six in ψ_1. Also, the fourth nucleon has to be in some other state ψ_2 which necessarily has much less binding energy than ψ'_1. Together with other effects which act in the same direction, this explains the non-existence of H^4 and Li^4: of course, if these nuclei existed they would show β-decay.

MESON THEORY

The exchange nature of nuclear forces is an attractive idea because it is closely related to meson theory. It is a general principle in elementary-particle physics that the forces between particles are associated with corresponding fields. For example, the force between two moving electrons is propagated by the Maxwell field; similarly the force between two nucleons is propagated by what we call the meson field. Another general principle states that these fields can also appear in the form of particles or quanta. For example, the Maxwell field has associated with it the photon—the quantum of electromagnetic radiation. In the same way the meson field has associated with it a new particle which we call the π-meson, or pion: it is the quantum of the meson field.

We now show how some of the simple properties of the meson field can be deduced. The Coulomb force between two charged particles is propagated by the electrostatic field $\varphi(x)$, which obeys Poisson's equation:

$$\Delta^2\varphi = -4\pi\rho \qquad \ldots.(3)$$

(where ρ is the charge density)

Yukawa suggested that the meson field $\psi(x)$, by which the force between two nucleons is propagated, obeys the equation

$$\Delta^2\psi - k^2\psi = -4\pi\sigma \qquad \ldots.(4)$$

(where σ is the nucleon density)

Here k^{-1} is a length; it is the range of nuclear forces, since the field $\psi(x)$ around a nucleon has the form

$$\psi(x) = e^{-kr}/r \qquad \ldots.(5)$$

Clearly k^{-1} must be somewhat greater than 10^{-13} cm to fit in with our ideas of nuclear forces.

Yukawa also discussed the new particle he would expect to be associated with this field ψ. The mass of this new particle is given by $m_\pi = kc/\hbar$. Taking $k^{-1} = 1{\cdot}4 \times 10^{-13}$ cm gives $m_\pi = 273 \times$ (electron mass). A particle with this mass, the π-meson, or pion, was subsequently discovered by Powell. We may say that the pion transmits the force between nucleons.

A simple theory shows how exchange forces occur between nucleons. Consider the interaction of a proton and a neutron; that part of ψ which relates to charged pions transfers the charge from one nucleon to another. In other words, the interaction interchanges the proton and the neutron. In a similar way the neutral pion can give an exchange force between two protons or two neutrons.

This simple theory is, unfortunately, far too crude to explain why the nucleon-nucleon force has a hard-core behaviour at short distance.

THE MAGIC NUMBERS

So far we have emphasized the obvious differences between nuclear structure and atomic structure; in particular, the saturation properties suggest a fairly homogeneous distribution of matter

throughout a large or medium nucleus. It is therefore a somewhat surprising fact that nuclei also show signs of a shell structure similar to the shell structure in atoms.

The simplest evidence for this shell structure comes from the anomalous properties of 'magic-number' nuclei; that is, nuclei which contain a magic number of neutrons or a magic number of protons: the magic numbers are 2, 8, 20, 28, 50, 82, 126. Magic-number nuclei have somewhat different properties from nuclei with neighbouring values of N or Z, and it would appear that the magic-number nuclei have in some way a completed shell structure, so that they are analogous to the inert gas atoms which have completed electronic shells.

There is considerable evidence for the magic numbers: the simplest piece of evidence is the number of stable nuclei which have a given value of Z or of N. One of the obvious symmetries in nuclei is that there are many more stable nuclei having even N- and even Z-values than of any other type. However, in addition to this there exist particularly many stable nuclei with the magic-number values of N or Z. For example, considering the values around $Z=20$ and $Z=50$, we have:

Element	A	K	Ca	Sc	Ti	V	Cr
Z	18	19	20	21	22	23	24
Stable isotopes	3	2	6	1	5	2	4

Element	Ag	Cd	In	Sn	Sb	Te
Z	47	48	49	50	51	52
Stable isotopes	2	8	1	10	2	8

Now look at the number of stable isotones, that is, nuclei with a given value of N. Around $N=20$ and $N=50$ we have:

N	18	19	20	21	22	48	49	50	51	52
Stable isotones	3	0	5	0	3	4	1	5	1	4

The binding energies also show definite discontinuities at the magic-number nuclei. Ca^{40} is a double-magic nucleus with $Z=20$ and $N=20$. The 20-proton configuration is obviously particularly stable, since we can add 8 more neutrons and still have a stable isotope Ca^{48}. This is the lightest stable isotope having N minus Z as large as 8; the next is Ni^{64}, which has the magic number $Z=28$. The lightest stable nuclei with N minus Z equal to 3 and 4 are Cl^{37} and S^{36} respectively; both have $N=20$, showing that the 20-neutron configuration is particularly stable.

There is much more evidence of this nature. It derives from such considerations as the binding energy of the last nucleon, the total abundance of isotopes in the earth, the number of β-unstable isotopes or isotones, the excitation energies of the first excited states of nuclei, the neutron capture cross-sections of nuclei, and the small departures of the radii of nuclei from formula (2). All of these point to the existence of fairly tightly bound closed shells of protons or neutrons in magic-number nuclei.

THE SHELL MODEL

The simplest way to explain the magic numbers is to forget most of what we know about the interaction of nucleons, and assume that each nucleon in the nucleus moves freely in an orbit about the centre of mass of the nucleus. This gives us the shell model of the nucleus.

Here it is useful to remember the shell structure of atoms. The number of electrons in the first five shells are as follows:

Shell	I	II	III	IV	V
States	$1s$	$2s$, $1p$	$3s$, $2p$	$4s$, $1d$, $3p$	$5s$, $2d$, $4p$
Electrons in shell	2	2, 6	2, 6	2, 10, 6	2, 10, 6
Electron total	2	10	18	36	54

The states are written down from left to right in the order of filling, so that in any given atom the binding energy of the states decreases from left to right. The inert gases He, Ne, A, Kr, Xe . . . occur at the closed-shell positions with 2, 10, 18, 36, 54 . . . electrons. The order of the levels depends on the nature of the force: in this case it is the electrostatic force.

An electrostatic force would not be appropriate for a nucleus. We assume that each nucleon moves freely in an orbit under the influence of the same attraction towards the centre of the nucleus. This attraction is supposed to be the average of the interaction of all the other nucleons with the nucleon in question. It turns out that an isotropic Hooke's-law force is a good approximation to this central attraction. This law of

force gives a new order of the levels, and we get the following shell structure for the neutrons (and of course the same shells for the protons):

Shell . .	I	II	III	IV	V
States . .	1*s*	1*p*	1*d*, 2*s*	1*f*, 2*p*	1*g*, 2*d*, 3*s*
Neutrons in shell . .	2	6	12	20	30
Neutron total	2	8	20	40	70

On this scheme, complete shells would contain 2, 8, 20, 40, 70 . . . neutrons, so that although the first three magic numbers are given correctly, the scheme subsequently goes wrong. Under the Hooke's-law force the states in each shell are degenerate, that is 1*d* and 2*s* have the same energy, and so on. Changing the law of force a little will avoid this degeneracy, but we cannot in this way get the correct magic numbers above 20. In figure 4 the 'square-well' potential results are shown.

Mrs Goeppert-Mayer, Jensen, and others showed how the correct scheme could be obtained if, in addition to the central force, each nucleon is subject to a spin-orbital force. This force preferentially aligns the spin of the nucleon in the same direction as its orbital angular momentum about the centre of mass of the nucleus. We know that this spin-orbital force exists because when protons or neutrons are scattered off nuclei they are polarized, that is, their spins are aligned as a result of the scattering. This scheme gives the correct shell structure for neutrons (or protons) (compare figure 4):

Shell . .	I	II	III	IV
States . .	1*s*	$1p_{3/2}$, $1p_{1/2}$	$1d_{5/2}$, 2*s*, $1d_{3/2}$	$1f_{7/2}$
Neutrons in shell	2	4, 2	6, 2, 4	8
Neutron total	2	8	20	28

Shell . .	V	VI
States . .	$2p_{3/2}$, $1f_{5/2}$, $2p_{1/2}$, $1g_{9/2}$	$1g_{7/2}$, $2d_{5/2}$, $2d_{3/2}$, 3*s*, $1h_{11/2}$
Neutrons in shell	4, 6, 2, 10	8, 6, 4, 2, 12
Neutron total	50	82

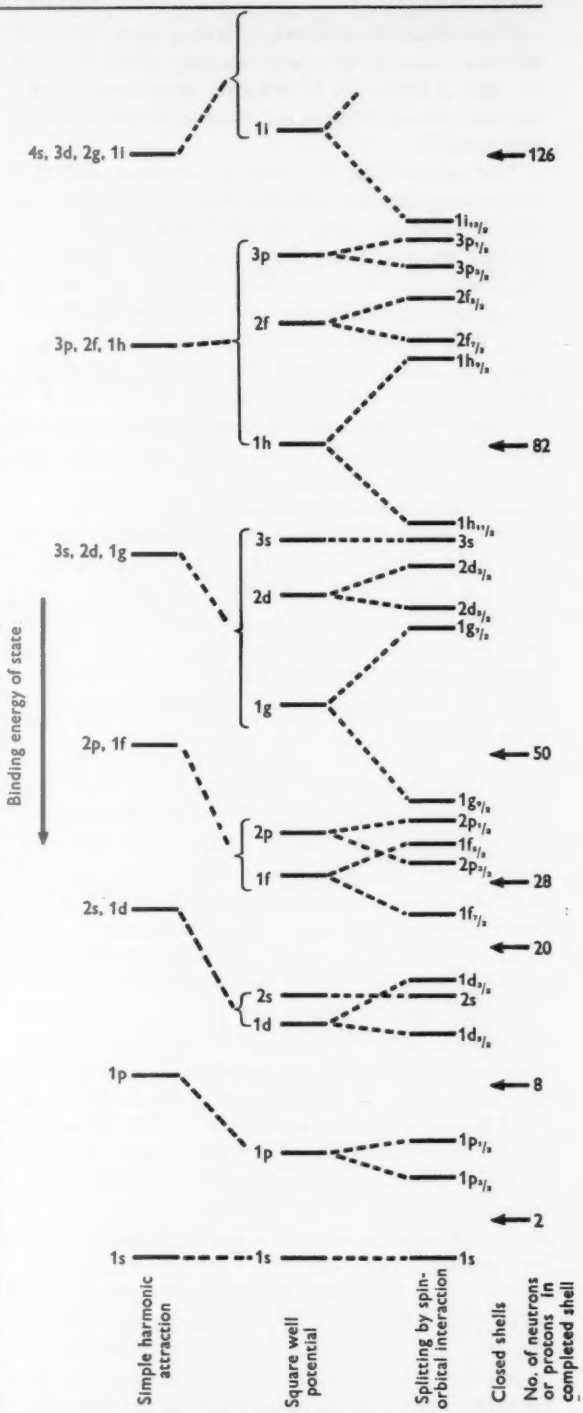


FIGURE 4 – *The nucleon energy-levels in the shell model. The columns show respectively* (a) *levels due to a Hooke's law attraction,* (b) *levels due to a square well,* (c) *the spin-orbital splitting. (The order of levels within the upper two shells is somewhat more complicated than that shown.)*

The subscripts such as 3/2 in $1p_{3/2}$ show the total angular momentum of the nucleon; thus $p_{3/2}$ and $p_{1/2}$ are p states in which the spin and orbital angular momentum are respectively parallel and anti-parallel.

The spin-orbital interaction increases with the orbital angular momentum value. Thus the $1p$ level is split into $1p_{3/2}$ and $1p_{1/2}$, which are close enough in energy to form one shell. Similarly $1d_{5/2}$ and $1d_{3/2}$ form one shell with $2s$. However, $1f_{7/2}$ is lowered sufficiently to form a new shell, and $1g_{9/2}$ is lowered so much that it joins the $2p_{3/2}$, $1f_{5/2}$, $2p_{1/2}$ shell. This scheme will give the magic numbers up to and including 126.

There are many simple and important deductions from the shell model. We give only one example. The nucleus B^{11} has $Z=5$, $N=6$. Hence its neutrons fill all the $1s$ and $1p_{3/2}$ states, while its protons fill the same states except for one $1p_{3/2}$ state. Therefore the nucleus B^{11} should have spin 3/2 and negative parity; this indeed is so. Similarly, the nuclei C^{13}, N^{15}, and O^{17} should have spins 1/2, 1/2, and 5/2 respectively; again experiments show this to be so. Many other far from trivial consequences of the shell model have been verified.

PHYSICAL BASIS OF THE SHELL MODEL

The most surprising fact about the shell model is that it makes any sense. Unlike the electrons in an atom, the nucleons cannot move around in orbits in the nucleus without frequently colliding with other nucleons. We would expect that when such collisions occur the colliding nucleons would be knocked out of their orbits.

For the shell model states $1s$, $1p_{3/2}$ . . . to be reasonably well defined, it is essential that a nucleon be able to make at least several circuits of its orbit before it is knocked out of the orbit. Now we have a paradox, as follows. The nucleons inside the nucleus have kinetic energies of 20–30 MeV. It is well known that if a nucleon whose kinetic energy is 20 or 30 MeV is shot into a nucleus it will be stopped in a very short mean free path, of the order of 10^{-13} cm in length. Indeed, Niels Bohr used this fact as the basis of his compound-nucleus model, by assuming that the incoming nucleon almost immediately shares all its kinetic energy with all the nucleons in the nucleus. It is therefore not easy to see how the shell-model states can exist.

Pauli's exclusion principle goes some way towards resolving this paradox. Each state in the nucleus can at most contain two neutrons and two protons, and in a nucleus which is not excited, all the states of lowest energy will be full. These form what is called the Fermi 'sea' of filled states (figure 5). If two nucleons in the nucleus collide, they cannot scatter each other into any states in the Fermi sea, since these states are already full. Therefore the nucleon-nucleon interaction produces very much less scattering between two nucleons which are in the nucleus than it will between two free nucleons. In the situation envisaged in the compound-nucleus model, the first stage is that the incoming nucleon collides with a nucleon in the Fermi sea and raises it to a state above the sea; this is allowed by the Pauli principle, so the interaction acts at full strength.

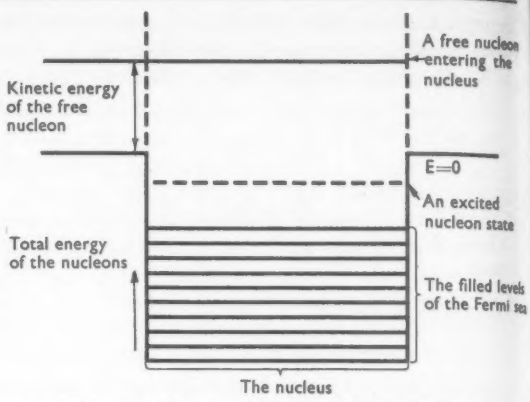

A free nucleon entering the nucleus
Kinetic energy of the free nucleon
E=0
An excited nucleon state
Total energy of the nucleons
The filled levels of the Fermi sea
The nucleus

FIGURE 5 – *The Fermi 'sea' of filled single-particle levels of a nucleus and a nucleon colliding with the nucleus.*

In this way we can see how the shell model could be reconciled with the strong nucleon-nucleon interaction. To do this properly, however, it will be necessary to use the many-body theory developed by Brueckner, which was mentioned earlier. This has not yet been done satisfactorily.

For the physicist there remain two difficulties:

(i) Some of the most valuable predictions of the shell model have to do with particles in levels just below the top of the Fermi sea: for example, the binding energy of the last nucleon and the spin of nuclei. Clearly, the exclusion principle is much less powerful in suppressing the undesirable effects of the nucleon-nucleon interaction for these states than it is for states which are deep in the Fermi sea.

(ii) What we have said about the use of the exclusion principle is really applicable to the longer-range attractive part of the

nucleon-nucleon interaction. The short range hard-core interaction must from time to time give rise to a scattering of nucleons in the Fermi sea in which there is a large momentum transfer, so that both nucleons are finally in states above the Fermi sea. It is necessary to understand why such collisions are not important in large nuclei.

BIBLIOGRAPHY

HULTHÉN, L. and SUGAWARA, M. 'The Two-Nucleon Problem' in 'Encyclopedia of Physics', Vol. XXXIX, pp. 1–143. Springer, Berlin. 1957.

ELLIOTT, J. P. and LANE, A. M. 'The Nuclear Shell Model', *ibid.*, pp. 241–410.

WEISSKOPF, V. F. *Science*, **113**, 101, 1951.

BRUECKNER, K. A. 'The Theory of Nuclear Structure' in 'The Many-Body Problem'. Methuen, London. 1958.

HUGENHOLTZ, N. M. and VAN HOVE, L. *Physica*, **24**, 363, 1958.

Book reviews

ASTROPHYSICS

Astrophysique générale, *by J. C. Pecker and E. Schatzman. Pp. x+756. Masson et Cie, Paris.* 1959. *Fcs.* 13 000.

Astrophysics is a subject that has developed with great rapidity and in many different directions during the past few decades. New results are continually being obtained that require modification of ideas that had been tentatively accepted. Many of the theoretical developments are in a state of flux. The literature of the subject, apart from scientific papers, has consisted of works of a more or less popular nature and of specialized treatises or monographs dealing with restricted aspects. There has been no comprehensive textbook of astrophysics suitable for students of physics, mathematics, and astronomy. Many discoveries in astrophysics have preceded, or have given birth to, important physical discoveries such as degenerate matter, spectra of highly ionized elements, thermonuclear reactions, and magnetohydrodynamics.

The authors have faced a difficult task in preparing an advanced textbook and have given an adequate presentation of both the observational and the theoretical developments up to a current date. Certain sections are necessarily highly mathematical, and the authors are to be commended for giving an index of the notations employed. In many books it is necessary to search back through many pages to find the definition of a symbol where it was first introduced.

The book is divided into five parts, each containing several chapters. In the first part, the basic physical ideas that are required are summarized. Then follows a section on instruments and methods of observation. The third part is concerned with the intrinsic properties of stars and the determination of these properties, including chapters on double stars, variable stars, and the internal structure of the stars. Systems of stars are dealt with in the fourth part; it includes consideration of galactic and globular clusters, stellar associations, the structure of the galaxy, interstellar matter, stellar evolution, and extragalactic systems. It is an unusual arrangement to find the Sun and the solar system relegated to the last section. The Sun is treated, however, as a typical star of class G2; the internal structure of the planets and the escape of atmospheres from them are among the subjects discussed.

The book, which has an excellent index of subjects and authors, can be highly commended. It is a valuable textbook and also a most useful reference book. H. SPENCER JONES

EXPERIMENTAL PHYSICS

Methods of Experimental Physics, *edited by L. Marton; Vol. I,* Classical Methods, *edited by I. Estermann. Pp. xii +596. Academic Press Inc., New York.* 1959. $12.80.

This book is the first volume of a series which (according to the foreword) 'should be a concise, well illustrated presentation of the most important methods or general principles, needed by the experimenter, complete with basic references for further reading'. It is divided into nine sections, dealing with evaluation of measurement, fundamental units and constants, mechanics of solids, mechanics of fluids, sound and vibration, heat and thermodynamics, optics, electricity, and magnetism, that is, the generally accepted branches of classical physics. Although it contains a mass of useful information, this reviewer considers that it has a number of serious faults. Far too much space is devoted to the description of well-established experimental methods and techniques which can be found in a host of existing books on physics. On the other hand, the newer methods which are scattered in journals and could most usefully be brought together in a critical way are dealt with very summarily and in many instances quite inadequately. No references are given to key papers or to authoritative recent reviews in several important fields of measurement. It seems very odd to include 25 pages on thermodynamics while omitting any reference to Moiré-fringe techniques for digitizing linear and angular measurement.

G. B. B. M. SUTHERLAND

HIGH-TEMPERATURE PHYSICS

Property Measurements at High Temperatures, *by W. D. Kingery. Pp. xii+ 416. John Wiley & Sons Inc., New York; Chapman and Hall Ltd, London.* 1959. *£6 12s. net.*

The increasing importance of high-temperature engines and manufacturing processes has led to an unprecedented demand for high-temperature materials and for data on high-temperature properties. This book deals with temperature measurement, furnaces, heat transport, the measurement of density, thermal expansion, mechanical, electrical, and magnetic properties, calorimetry, and phase equilibria, and includes a brief treatment of chemical thermodynamics and kinetic measurements at high temperature. Dr Kingery writes with clarity and authority on this wide range of topics.

Each chapter begins with a concise account of the basic principles of the

property being considered. This is very useful as a refresher course, although inadequate unless the reader has some previous knowledge of the subject. Then follows a careful description of experimental methods for measurement of the property. The numerous diagrams of apparatus are particularly clear; there is a good index. The volume is one which will be welcomed by those whose work is concerned in any way with temperatures above 1400° C. G. PORTER

ELECTRON PHYSICS

Electron Physics—the Physics of the Free Electron, *by O. Klemperer. Pp. xi + 248. Butterworths Scientific Publications, London; Academic Press Inc., New York.* 1959. 32*s.* 6*d. net.*

This book has grown out of courses of lectures on electron physics given by the author. It covers a rather wider range than is implied by its subtitle, 'The Physics of the Free Electron', for it discusses such topics as Larmor's theorem, paramagnetism, and the Zeeman effect, which are essentially properties of bound electrons. On the whole, however, it adheres to the limits it has defined. After a historical introduction, it sets out to describe the motions performed by electrons in combinations of electric and magnetic fields, leading on naturally to electron optics and the characteristic properties of simple electron-tubes, with particular reference to space-charge effects. There is a simple but adequate treatment of noise and fluctuation effects. A chapter is devoted to methods of detecting electrons.

The second part of the book is devoted to what are physically more fundamental aspects of electrons. There are chapters on methods of determining their charge and the charge/mass ratio, on the relativistic dynamics of electrons, on their wave nature, and on the spin and associated properties of electrons.

Some of the later chapters could be criticized for not being well informed, such as the discussion of electromagnetic mass and the description of magnetic resonance. If read as a guide to the subject, however, the book should be very useful, particularly to undergraduates in physics and electrical engineering. M. H. L. PRYCE

COLLOID CHEMISTRY

Introduction to Colloid Chemistry, *by Karol J. Mysels. Pp. xv+475. Interscience Publishers Inc., New York; Interscience Publishers Ltd, London.* 1959. 75*s. net.*

Dr Mysels is an active experimental worker and teacher in the field of colloid chemistry, and consequently we might expect that an original treatment of the subject would result when he puts pen to paper. In this we are not disappointed. Textbooks on the subject of colloid chemistry are usually based on one or other of two fundamental philosophies, either that colloid chemistry involves the preparative and descriptive fields associated with the names of the early workers such as van Bemmelen, or that the interphase, with its properties, is the cornerstone of the subject. This view was first presented in great clarity by Freundlich, and has been subsequently followed by such authorities as Irving Langmuir and N. K. Adam.

Dr Mysels has chosen to construct his book with the concept of the 'particle' as the central theme of what is essentially the elementary physical chemistry of particles. This approach has certain advantages, for it permits the reader versed in the physical chemistry of small molecules to appreciate to the full those sections of the book dealing in an elementary manner, with colligative properties, diffusion, and sedimentation. On the other hand, the interesting and important properties of interfaces receive but little attention. For example, I have failed to find the name of Willard Gibbs mentioned in any context. Nevertheless the book contains a very readable account of the colloid state, included in which are the polymers, which may serve as a corrective to the devoted followers of the Freundlich school. To many readers, at least in Britain the use of German script symbols for various concentrations is confusing and the explanation of some effects, such as osmotic pressure, hardly satisfactory.

The book is very clearly written with excellent explanatory diagrams, and print and binding are up to the high standard set by Interscience Publishers. ERIC K. RIDEAL

CHROMATOGRAPHY

Handbuch der Papierchromatographie. *Vol.* I, Grundlagen und Technik, *edited by I. M. Hais and K. Macek. Pp. xxiv+860. VEB Gustav Fischer Verlag, Jena* 1958. *DM* 58.40.

This is Volume I of an extensive treatise on paper chromatography edited by two distinguished Czech workers in this field. The chapters are written by these workers alone or in association with others, so that the poor correlation often arising from a variety of authors is avoided. Hais, for example, after opening the book with a summary of the history of the technique gives, in association with two co-workers, a chapter on the theoretical and practical basis of chromatography.

In the experimental section, the deionizing of solutions, sample application, and choice of paper are dealt with first. The physical characteristics of papers produced by the major manufacturers are described, and a photographic comparison is given of a separation of identical mixtures of amino acids carried out on each of these papers.

Adequate coverage is given of the properties of the common organic solvents, and methods are outlined for the identification of structural groups on the basis of chromatographic behaviour. Unfortunately, little space is devoted to molecular interactions in solution, but this is a common fault in all books on chromatography. However, the authors do provide a list of ten solvent-systems whose systematic use provides a basis for working out a system for hitherto unresolved mixtures.

Apparatus is covered in a short but concise section and is followed by a useful discussion on factors affecting zone shape and R_f. Subsequent chapters deal with detection, quantitative estimation, and special techniques for radioactive substances. These general sections occupy roughly one-third of the book; the remainder deals with specific groups of substances (and their derivatives) ranging from alcohols to synthetic dyestuffs and inorganic substances. The appendix includes information on spray and dip reagents, paper impregnation, and specific instructions for preparation of derivatives.

R_f values are listed on a vertical scale by a spot alongside the name of the substance and so provide an immediate visual impression of the ease or difficulty of a given separation. Only one criticism can be levelled, in that too much use is made of photographs of chromatograms, and this must have materially added to the cost of the book. Since the literature appears to have been covered up to 1956, the inclusion of detailed author and subject indexes makes this an invaluable reference book for all laboratories using paper chromatography. A. T. JAMES

INDUSTRIAL CHEMISTRY

Electrolytic Manufacture of Chemicals from Salts, *by D. W. F. Hardie. Pp. xii +74. Published for Imperial Chemical Industries Ltd, London, by Oxford University Press, London.* 1959. *7s. 6d. net.*

This is the third in a series of textbooks sponsored by Imperial Chemical Industries Ltd, and designed to bridge the gap between the chemistry taught at school and that practised in industry. As the author states in his introduction, the electrolytic processes starting from salt lend themselves particularly well to such an approach. The underlying physical chemistry has considerable interest in itself, yet is easily understood by the intelligent sixth-former; moreover, it is readily related to the power requirements and general economics of the industry.

A good account is given of such electrochemical concepts as decomposition voltage and current efficiency, and the various components of the working voltage are set out very clearly; the reviewer was surprised to learn what a high percentage of this voltage is required, in the Downs sodium cell, simply to overcome the resistance of the electrical connections. The distinction between heats and free energies of formation might, however, have been stressed in the text instead of being merely mentioned in a footnote.

In a further chapter, the mercury cell is described in some detail, as are two forms of diaphragm cell and the Downs sodium cell. Other chapters deal with the physical properties and uses of the various products, with their packing and transport, with production statistics, and with the historical development of the processes. A chronology of the development of the industry and a useful glossary of technical terms form two appendices, and there is also a bibliography.

This book can be thoroughly recommended for school and university libraries. J. E. SPICE

CRYSTALLOGRAPHY

International Tables for X-ray Crystallography, *Volume II*, Mathematical Tables, *edited by John S. Kasper and Kathleen Lonsdale. Pp. xviii+444. Published for the International Union of Crystallography by The Kynoch Press, Birmingham.* 1959. *£5 15s. net.*

Crystallographers are again indebted to a group of distinguished authors for a most useful aid. Volume II of the 'International Tables' is restricted to mathematical information. Formulae, tables of functions, and diagrams used in many stages of a crystal-structure determination are given in convenient forms.

A special chapter summarizes mathematical techniques of special interest in X-ray crystal structure analysis. He will be a rare crystallographer who finds no use for this well-ordered reminder of things that he may once have studied but no longer recalls accurately.

The main sections deal with crystal geometry, diffraction geometry, the physics of diffraction methods, Fourier theory with special attention to Fourier transforms, and structure factors. Throughout, carefully selected references are given. The production by The Kynoch Press is of the same excellent quality as that of Volume I. A few errors are unimportant.

For a standard work, words should be chosen carefully. Generally this has been done, but there are points at which simplification of the style would have made the meaning clearer. H. M. POWELL

RADIOBIOLOGY

Strahlenbiologie. Grundlagen und Ergebnisse, *by H. Fritz-Niggli. Pp. xvi +380. Georg Thieme Verlag, Stuttgart.* 1959. *DM* 65.

Radiobiology, like cancer research, covers almost every subject that anyone might wish to work on, and a comprehensive book on it is therefore difficult to write; Professor Fritz-Niggli has, however, tackled the problem with courage and success. The book is divided into sections on physics, chemistry, biochemistry, genetics, cells and cell particles, embryos, regeneration, cancer, pathology and death, sickness, prophylaxis and therapy, and theories. The distribution corresponds with the title, in that the more biological parts, such as genetics, receive the longest and most advanced treatments; but a little more detail in parts such as that on prophylaxis would have been welcome. For example, if the table of protective substances included some measures of their effectiveness, it might help to debunk some of the high-pressure salesmanship that has surrounded some of them. Most of the copious tables, diagrams, and illustrations are very pleasing and informative, and little of value in radiobiology has escaped the author's attention. J. ST. L. PHILPOT

BIOLOGICAL TECHNIQUES

Tools of Biological Research, *edited by H. J. B. Atkins. Pp. xvi+183. Blackwell Scientific Publications, Oxford.* 1959. *37s. 6d. net.*

These descriptions of special methods used in biological research are based on papers given at a symposium held at Guy's Hospital in October 1958 under the guiding hand of the editor, acting for the Surgical Research Society. After an introduction by the President of the Royal Society and an article on the design of experiments, there are nine short accounts of techniques. Two are biological in nature: tissue culture and tissue transplantation. The others are physical: flame photometry, electromanometry, electron microscopy, phase and interference microscopy, electrophoresis, X-ray-image intensification, and mass spectrometry. All are by active practitioners of the subjects; the chapters are well illustrated and include lists of selected papers for further reading. Mostly they are 10–15 pages in length, and thus can be little more than a statement of principles of operation and an outline of the range of applications. The main exception is the article on electron microscopy, which in 50 pages gives as clear and concise an account as could be wished of almost all aspects of the subject. With one exception, the contributions are by authors who either have medical qualifications or are working in biological laboratories, so that attention to the needs and background of the 'consumers' is guaranteed. All in all, it would be difficult to find a better introduction to some of the new techniques which are now finding use in biological and medical research. V. E. COSSLETT

PLANT PHYSIOLOGY

Plant Physiology, *Vol. II*, Plants in Relation to Water and Solutes, *edited by F. C. Steward. Pp. xvii+758. Academic Press Inc., New York.* 1959. $22.

It has been common knowledge among botanists for thirty or forty years that the major branches of their science have become too large and varied for reasonably detailed treatment by a single writer. 'Recent advances', treatises, and encyclopaedias, running sometimes to many volumes, are therefore the fashion. Each volume is liable to contain chapters written by a number of different experts with whatever degree of co-ordination may be attainable. In the actively developing sector of botany covered by the present treatise, difficulties of size are

supplemented by those of tempo and even of taste; there are very few problems of plant physiology which at present have universally accepted solutions. Three of the independently written chapters of this volume have occasion to discuss the relative permeability of the inner and outer layers of plant protoplasm. The first 'inclines to the classical view' that the two membranes are similar in their permeability towards solutes, while the second accepts the idea that the inner is much the more impermeable barrier. The discussions in the remaining chapter do not reveal its author's personal beliefs to this reviewer.

Nearly all the authors writing in this, the second (but first to appear) of the six projected volumes, are veterans in their own fields and have learnt the hazards of dogmatic statement in plant physiology. The general attitude is that of looking round the corner rather than that of blazing a trail.

For advanced and post-graduate students liking their information to be available between at least a limited number of covers this volume will be very helpful for the next five years.

W. O. JAMES

CARCINOGENIC COMPOUNDS

Bibliography of Cancer produced by Pure Chemical Compounds—A Survey of the Literature up to and including 1947, *by O. Neubauer. Pp. xxvii+604. Clarendon Press; Oxford University Press, London.* 1959. 42*s.* net.

Dr Neubauer compiled this bibliography at the suggestion of the doyen of cancer research—the late Sir Ernest Kennaway.

The book is based on 5000 papers which had been published up to 1947 and which referred to cancer-producing chemical compounds; to obtain the authors and titles to the papers, Neubauer worked through nearly 500 journals. Having secured his material, the problem was to present it as a well-integrated encyclopaedia and not as a mere catalogue; his method has been, first, to arrange the 5000 papers in alphabetical order of authors, giving author, date, full title of paper, and a reference number. This forms the first part of the book. The second part, and the far more difficult section to arrange, comprises a system whereby the papers are divided into classes according to subject such as chemical properties of the carcinogens, their physical properties, mode of administration, local effect on skin, internal organs, or distant tissue, their metabolism, genetic or immunity effects, and other numerous characteristics, making in all 32 categories. These are again subdivided, in another plane as it were, into those dealing with carcinogenic compounds belonging to the class of polycyclics, azo compounds, sterols, and other orders of chemical constitution. In each sub-group the appropriate members of the 5000 papers are again rearranged in chronological order, and Neubauer has achieved the ultimate degree of compression by using a summary of two words only.

The bibliography will be of most use to those who are already acquainted with this field of work and who need a ready-reference system based on authors' names, and giving titles, dates, and journal details. Unfortunately the book cannot be considered a complete success, firstly because it stops at 1947, and secondly because of the inadequate indexing. A work of reference depends for its efficiency on its indexing system. The bibliography would have been vastly improved by a very full and properly assembled set of indexes employing detailed cross-references.

I. HIEGER

VETERINARY SCIENCE

Research in Veterinary Science, *Vol. I, No. 1, January 1960. Pp. iv+93+x. Blackwell Scientific Publications, Oxford. Quarterly,* 25*s. Annual subscription* 90*s. net.*

The appearance of the first issue of 'Research in Veterinary Science' marks an important advance in veterinary literature. In the foreword, the President of the British Veterinary Association explains the high purpose of this journal, and the first issue augurs well for the fulfilment of those high ideals. The contributions to this first issue cover a wide selection of animals, including poultry, cattle, pigs, and dogs, and will provide valuable information for research workers in many disciplines. The authors of the several contributions are to be congratulated on the clear and easy style with which they write and on the excellence of the diagrams, photographs, and photomicrographs which are used in illustration of the text. The references given at the end of each article are well chosen and fully adequate, without being unnecessarily exhaustive. The presentation of the new publication is pleasing in appearance, dignified, and a credit to those responsible for its production. The long-felt need for a journal of this type now appears to have been met, and veterinary research workers throughout the world will acclaim 'Research in Veterinary Science' as a most valuable acquisition.

H. BURROW

THE NEWTON LETTERS

The Correspondence of Isaac Newton, *Vol. I,* 1661–1675, *edited by H. W. Turnbull. Pp. xxxviii+468. Cambridge, published for the Royal Society at the University Press, London.* 1959. £7 7*s. net.*

It has long been a matter for reproach that no uniform critical edition of all Newton's writings exists. Plans to make good this deficiency have always foundered under the sheer bulk and complexity of Newton's literary remains, swollen by his chemical and theological manuscripts to some three and a half million words.

In 1939 the Royal Society persuaded the late Professor H. C. Plummer to attack the more feasible task of editing the Newton correspondence, and a good start was made In 1947, following the death of Professor Plummer, the editorship passed to Professor H. W. Turnbull, who has substantially completed the editing of the first three volumes of the series. The aim has been to print *in extenso* all known letters written by, or addressed to, Newton, together with extracts from his personal memoranda and from contemporary letters touching on his work.

This first volume, to which Professor Andrade has contributed a scholarly introduction, is of particular interest, for it embraces the discovery of the composite nature of sunlight, the construction of the reflecting telescope, the early experiments on fluxions and quadratures, and even some foretaste of celestial mechanics. Latin texts are translated into English, and technical or historical points calling for elucidation are scrupulously dealt with in the accompanying notes. Their scientific interest apart, these letters throw light on Newton's character and on his relations with other men of science. The plates include specimen pages from Newton's letters and manuscripts of the period; Kneller's portrait forms the frontispiece.

This superbly produced volume worthily commemorates the Tercentenary Year of the Royal Society; the appearance of its successors will be eagerly awaited by students of Newton and of his age.

A. ARMITAGE

Short notices of books

(These notices are descriptive rather than critical and are designed to give a general indication of the nature and scope of the books.)

Data for Biochemical Research, *edited by R. M. C. Dawson, D. C. Elliott, W. H. Elliott, and K. M. Jones. Pp. xiii+299. Clarendon Press, Oxford; University Press, London.* 1959. 63*s. net.*

The aim of this book is to provide factual information about the compounds, reagents, and techniques that biochemists use in their everyday research. So as to keep the size of the book to a minimum, the editors have adopted the principle that all the information in the book should be useful in the laboratory. The subjects covered include biochemical compounds, buffers and physiological media, ion-exchange resins, isotopic data, and manometry. References are given so that further information may be found.

Cell Organism and Milieu, *edited by D. Rudnick. Pp. v+326. The Ronald Press Co., New York.* 1959. $8.

The theme of the seventeenth symposium of the Society for the Study of Development and Growth was that of 'differentiation and growth in response to a changing chemical environment'. The contributions to the symposium are published in this book, and include papers on the role of cell structures in cell movements, the chemistry and physiology of insect growth-hormones, the experimental modifications of development in the root, and the physiology and biochemistry of the mammalian blastocyst.

Radiation Biology of *Vicia Faba* in relation to the General Problem, *by J. Read. Pp. xxii+270. Blackwell Scientific Publications Ltd, Oxford.* 1959. 45*s. net.*

Radiation biologists have probably a wider knowledge of the effect of ionizing radiations on the root of the broad bean *Vicia faba* than on any other living material. This information is surveyed in this book in such a way as to give an introduction to the whole subject of radiation biology. An attempt is made to identify and explain the most important damage sustained by the cells of the root, and to suggest the extent to which conclusions based on *Vicia faba* can be applied generally to animal and human tissues.

Vitamin B_{12}, *by E. Lester Smith. Pp. xii+196. Methuen & Co. Ltd, London; John Wiley & Sons Inc., New York.* 1960. 15*s. net.*

This book is intended for the biochemist, and gives an account of the research that led to the isolation of vitamin B_{12}, as well as describing its chemistry, its part in animal and human nutrition, and the mechanisms of its action. Other subjects covered include the origin and distribution of the vitamin, and its assay.

Modern Coordination Chemistry, *edited by J. Lewis and R. G. Wilkins. Pp. xvi+487. Interscience Publishers Inc., New York; Interscience Publishers Ltd, London.* 1960. 80*s. net.*

The physical methods of co-ordination chemistry and their underlying principles are dealt with in this book. The subjects covered include the reaction rates of transitional metal complexes, the isomers of complex compounds, the visible and ultra-violet spectroscopy of complex compounds, and their magnetochemistry.

International Conference on Coordination Chemistry. *Pp. 204. The Chemical Society, London.* 1959. 42*s. net.*

The lectures delivered at the conference held in London in April 1959 are published in this volume, together with abstracts of the papers that were submitted. The lectures covered, among other subjects, the stability of metal complexes, the mechanism of complex-ion reactions, metal-ligand bonds, and complex acetylides of transition metals.

Nouveau traité de chimie minérale, *edited by P. Pascal. Vol. XVIII. Pp. xl+944. Masson et Cie, Paris.* 1959. *Paper covers, NFcs* 95; *bound, NFcs* 107

Although this volume is specially concerned with the complexes of iron, cobalt, and nickel, the chapter on the complexes of iron, by C. Duval, also includes an account of the iron salts. Other sections deal with the carbonyls and nitrosyls of iron by A. Michel, the cobalt complexes and carbonyls by, respectively, P. Job and J. Amiel, and the complexes and carbonyl of nickel by Madame C. Duval and P. Pascal.

Heterocyclic Chemistry, *by A. R. Katritzsky and J. M. Lagowski. Pp. 274. Methuen & Co. Ltd, London; John Wiley & Sons Inc., New York.* 1960. 21*s. net.*

The authors of this book aimed at producing a treatment of heterocyclic chemistry in terms of electronic theory that would be useful to the advanced student and the junior research worker. The book is a survey of the whole of basic heterocyclic chemistry; it emphasizes the correlations between the methods of preparation and the properties of the various ring systems.

Cahiers de synthèse organique, *Vol. V, by J. Mathieu and A. Allais. Pp.* 394. *Masson et Cie, Paris.* 1959. *Paper covers, NFcs* 78; *bound, NFcs* 85.

Volume v of this work—it is to be completed in seven volumes—is concerned with degradation reactions. These are not considered as methods of determining the structures of compounds but as complements to synthetic methods of preparation. The book is divided into two sections, one dealing with reactions in which a carbon-containing group is removed, the other with reactions in which a carbon chain is broken or a ring opened. The work is intended to be used by organic chemists as a guide to preparative methods.

Structure Reports for 1952, *Vol. XVI, edited by A. J. C. Wilson. Pp. viii+651. Published for the International Union of Crystallography by A. Oosthoek's Uitgevers Mij, Utrecht.* 1959. *Fl.* 120.

It is the intention of this book to present all of the material of structural interest that is contained in a published paper while giving, at most, a brief reference to the rest of the contents. It is divided into three sections, devoted to metals, edited by N. C. Baenziger, to inorganic compounds, by J. Wyart, and to organic compounds, by J. Monteath Robertson. The volume includes a comprehensive set of indexes to facilitate reference to a particular substance.

Notes on contributors

W. L. BARGMANN,
Dr. Med.,
Was born in 1906 at Nürnberg and in 1935 joined the staff of the University of Zürich. Later he was prosector and departmental head in Leipzig and Königsberg. After the war, in 1945, he went to Göttingen, and since February 1946 he has been the director of the anatomy department at the University of Kiel. He has studied numerous histological and micro-anatomical problems, mainly in the fields of endocrinology and neurohistology. He has also published studies of anatomy and art, Goethe and morphology, and a textbook of histology. He edits *Zeitschrift für Zellforschung und mikroskopische Anatomie* (together with J. Seiler), the *Handbuch der mikroskopischen Anatomie des Menschen* and *Zwanglose Abhandlungen aus dem Gebiete der normalen und pathologischen Anatomie* (together with W. Doerr).

N. L. PADDOCK,
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Was born in Bristol in 1918 and educated at Colston's School, Bristol, and, after wartime service in the R.A.F., at Emmanuel College, Cambridge. After a period of research at Cambridge, he joined Albright and Wilson, Ltd, at Oldbury, where he is now Head of the physical chemistry section of the Research Department. His main research interests are physical and theoretical methods in inorganic chemistry, and the application of physical chemistry to chemical engineering problems.

H. PETTERSSON,
For. Mem. R.S.,
Was born in 1888 and studied physics under K. Ångström in Uppsala and Sir William Ramsay in London. He became Reader in oceanography at Gothenburg in 1914, and professor there in 1930, and has been director of its Oceanographic Institute since its foundation in 1939. He was the leader of the Swedish circumnavigating deep sea expedition aboard the *Albatross*, 1947–48. He has carried out research in physics and oceanography and has constructed various instruments, among others a quartz-fibre microbalance (1914).

W. WILLIAMS,
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Was born in Cardiganshire in 1920 and was educated at Aberaeron Grammar School and Aberystwyth College, University of Wales. From 1942 to 1950 he was engaged in research on genetics and on the breeding of herbage grasses and legumes at the Welsh Plant Breeding Station. In 1950 he was appointed lecturer in Agricultural Botany at King's College, Newcastle-upon-Tyne, in the University of Durham. Since 1955 he has been Head of the Department of Plant Breeding at the John Innes Institute, Bayfordbury, Hertfordshire. His research studies comprise incompatibility systems in plants, disease resistance, and the inheritance of quantitative characters.

A. G. BROWN
Was born in Montrose in 1910. For the past 25 years he has been on the staff of the John Innes Institute. He was concerned with M. B. Crane in studies on pollination of fruit species which led to important advances in the design of commercial orchards. He has been responsible for the breeding of several new varieties of tree fruits, and is at present engaged in developing disease-resistant varieties of apples.

D. A. PARRY,
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Studied zoology at Bristol and Cambridge Universities. During the war he was concerned in liaison work between radar scientists and the R.A.F., and in operational research. Afterwards he joined an Antarctic whaling expedition on behalf of the Discovery Committee and spent the following three years studying cetacean mechanics. Since 1950 he has been interested in mechanical problems connected with terrestrial arthropods, particularly spiders. He is a lecturer in zoology at Cambridge University, and a tutor and Fellow of King's College.

J. HAMILTON,
M.A., Ph.D.,
Was born in 1918 in Sligo, Ireland, and educated at the Royal Academical Institution, Belfast, the Universities of Belfast and Manchester, and the Institute for Advanced Studies, Dublin. During the war he worked in naval operational research in England and South East Asia; from 1948 to 1949 he was a lecturer in Theoretical Physics at Manchester University. He is at present a lecturer in mathematics at Cambridge University and a Fellow of Christ's College, Cambridge.